Advanced Synthesis & Catalysis

Supporting Information

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General information

The cycloaddition reactions were performed in 1-dram borosilicate glass vials, which were irradiated with blue LED light from a distance of 12 cm. Detailed specifications of the blue light source are given below. The NMR spectra were recorded on a Bruker Ascend 400 (400 MHz) spectrometer. Chemical shifts are given in parts per million (δ) downfield from tetramethylsilane as the internal standard. Deuterochloroform was used as a solvent, unless otherwise stated. Mass spectral data were recorded using LTQ Orbitrap XL. IR spectra were recorded on an IR Thermo Scientific NICOLET iS10 (4950) spectrometer. Flash chromatography employed silica gel 60 (230–400 mesh) while thin layer chromatography was carried out using alumina plates with a 0.25 mm silica layer (Kieselgel 60 F254, Merck). Compounds were visualized by staining with potassium permanganate solution. The solvents were purified by distillation before use.

Blue LED light specification:

- Manufacturer Hennessy Lighting Technology Co., Ltd.
- Length 10m, Width 8mm (Figure 1S)
- LED Chip Model: SMD3528,
- Voltage: 12V DC,
- Power 4.8 W,
- Wavelength of 465mm (+/-5nm)

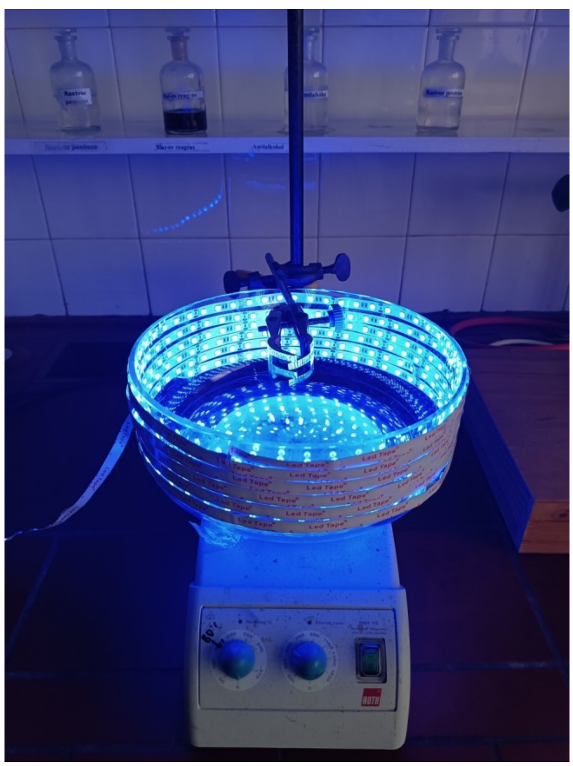
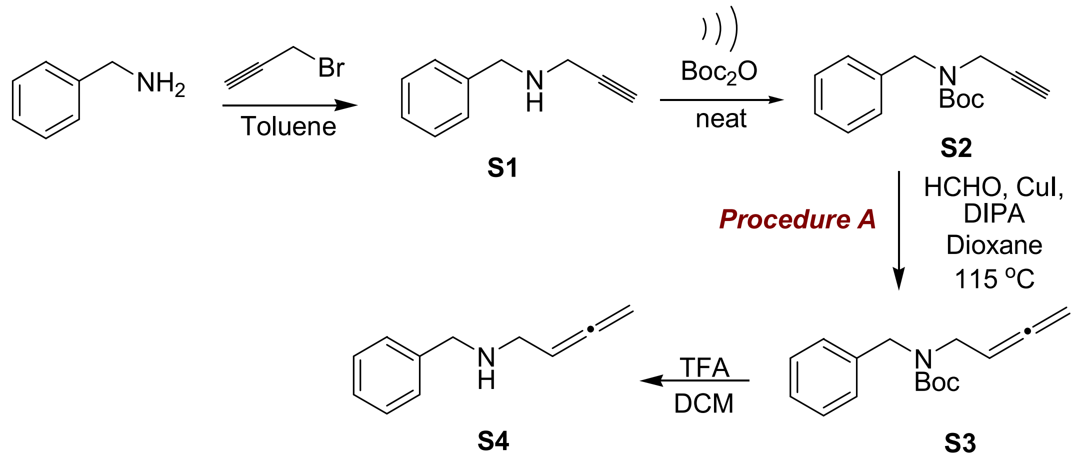
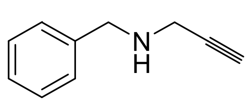


Figure 1S. Experimental setup for cycloaddition reaction.

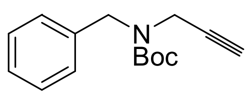
Synthetic procedures



Scheme 1s

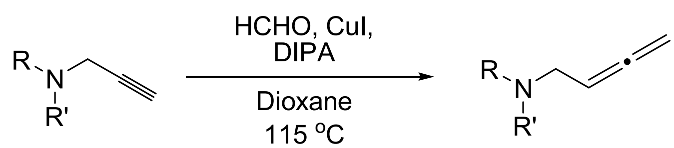


N-benzylpropargylamine (S1) Propargyl bromide (1.5 mL - 80 wt.% solution in toluene, 14 mmol) was slowly added to a solution of benzylamine (7.63 mL, 70 mmol) in toluene 10 mL. The resulting mixture was stirred at room temperature for 18 hours. Reaction mixture was diluted with ether and washed with saturated $NaHCO_3$ (3 × 20 mL). The organic phase was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Crude oil was purified by silica gel column chromatography (PE/EtOAc = 3/1) to afford **S1** in 86 % yield as a brown oil (1748 mg, 12.04 mmol). The spectral data are consistent with those reported in the literature.[1]

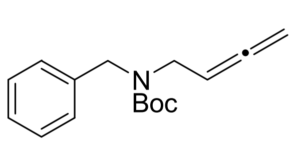


N-Boc-N-benzylpropargylamine (S2) A round-bottom flask containing **S1** (1748 mg, 12.04 mmol) was placed in a sonicator bath. Boc-anhydride (2756 mg, 12.64 mmol) was added dropwise over the course of 15 minutes into the round-bottom flask containing N-benzylpropargylamine. The reaction was completed after 30 minutes (monitored by TLC). Crude mixture was purified by silica gel column chromatography (PE/Et_2O = 8/2) to afford **S2** in 90 % yield as a white amorphous solid (2656 mg, 10.84 mmol). The spectral data are consistent with those reported in the literature.[2]

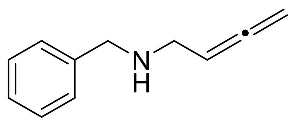
General procedure A



To a stirred solution of desired propargyl amide (1 equiv.) in dioxane (20 mL) under nitrogen atmosphere, paraformaldehyde (0.5 equiv), copper(I) iodide (2.5 equiv.) and diisopropylamine (DIPA) (2 equiv) were added. The reaction mixture was stirred at reflux overnight. Reaction mixture was thereafter concentrated under reduced pressure. Crude oil was purified by silica gel column chromatography to afford the desired allenamide.[3]

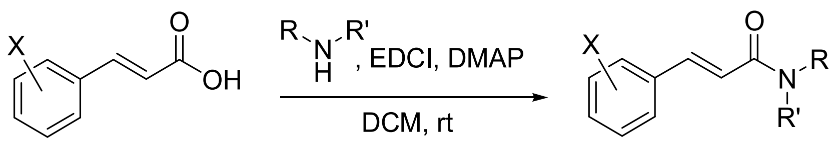


***tert*-butyl benzyl(buta-2,3-dienyl)carbamate (S3)** The general procedure A was followed using **S2** (2656 mg, 10.84 mmol). Purification by silica gel column chromatography (PE/Et_2O = 8/2) afforded **S3** (2.021 mg, 7.80 mmol) as a white amorphous solid. The spectral data are consistent with those reported in the literature.[2]

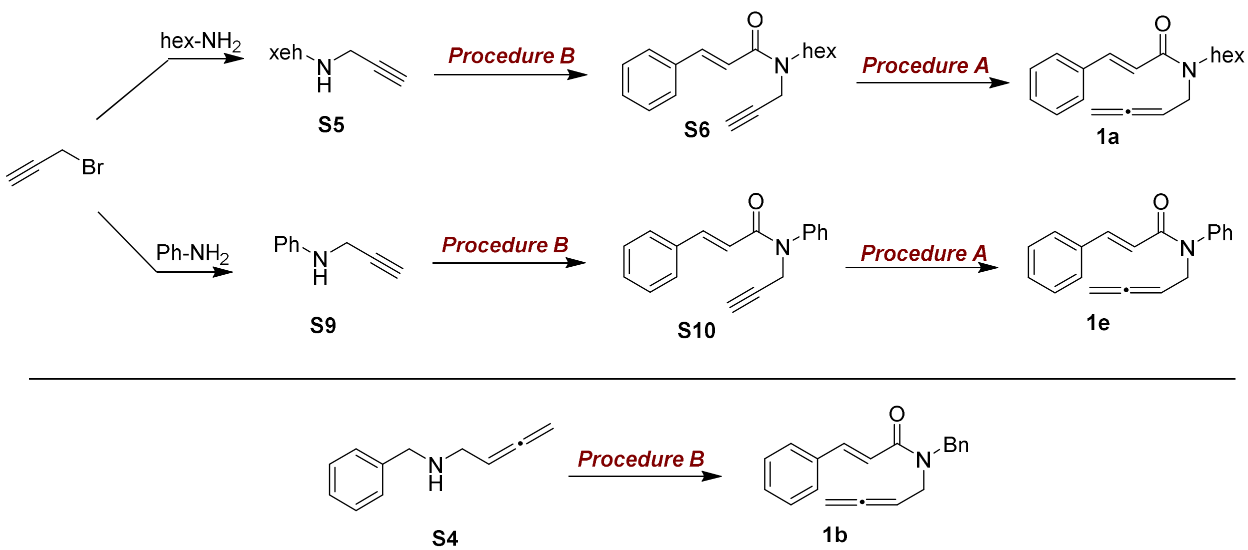


N-benzylbuta-2,3-dien-1-amine (S4) To a stirred solution of **S3** (2.021 mg, 7.80 mmol) in dichloromethane (30 mL), trifluoroacetic acid (8mL, 47 mmol) was added. The reaction mixture was stirred at room temperature for 2h. Reaction mixture was thereafter washed with saturated $NaHCO_3$ solution (3 x 20 mL). The organic phase was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to afford **S4** in 90 % yield as a brown oil (1116 mg, 7.02 mmol). The spectral data are consistent with those reported in the literature.[2]

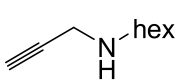
General procedure B



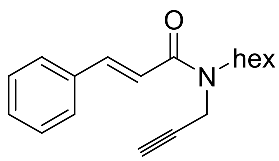
To a stirred solution of desired cinnamic acid (1 equiv) in anhydrous dichloromethane (2 M), under nitrogen atmosphere, EDCI (1.2 equiv), and DMAP (1.2 equiv) were added. The resulting mixture was stirred at room temperature for 5 minutes before adding desired amine (1.2 equiv). The mixture was thereafter stirred overnight at room temperature. Reaction mixture was thereafter concentrated under reduced pressure. Crude oil was purified by silica gel column chromatography (PE/Et_2O) to afford desired amide.



Scheme 2s



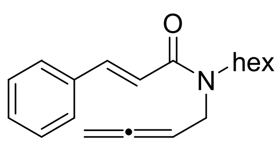
***N*-hexylcinnamamide (S5)** To a stirred solution of hexylamine (203.7 mg, 2.02 mmol) in DMF (10 mL) potassium carbonate (139.2 mg, 1.01 mmol) and propargyl-bromide (80% solution in toluene) (47.7 µL, 0.5 mmol) were added. The reaction mixture was stirred overnight at room temperature. Reaction mixture was thereafter diluted with diethyl-ether (30 mL) and washed with water (4 x 20 mL). The organic phase was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Crude oil was purified by silica gel column chromatography (PE/EtOAc = 4/1) to afford **S5** in 92 % yield as a brown oil (63.9 mg, 0.46 mmol). The spectral data are consistent with those reported in the literature. The spectral data are consistent with those reported in the literature.[4]



***N*-hexyl-*N*-(prop-2-ynyl)cinnamamide (S6)** The general procedure B was followed using cinnamic acid (50 mg, 0.38 mmol) and **S5** (56.4 mg, 0.41 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/1) afforded **S6** (90.1 mg, 0.34 mmol) as a brown oil in a 89% yield as a mixture of rotamers (66:34).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 15.7 Hz, 1$H_{\text{both rotamers}}$), 7.52 (d, *J* = 5.5 Hz, 2$H_{\text{both rotamers}}$), 7.43 – 7.32 (m, 3$H_{\text{both rotamers}}$), 6.92 (d, *J* = 15.2 Hz, 1H_{minor}), 6.82 (d, *J* = 15.3 Hz, 1H_{major}), 4.33 (s, 2H_{major}), 4.16 (s, 1H_{minor}), 3.55 (t, *J* = 7.3 Hz, 2$H_{\text{both rotamers}}$), 2.34 (s, 1H_{minor}), 2.22 (s, 1H_{major}), 1.77 – 1.65 (m, 2$H_{\text{both rotamers}}$), 1.40 – 1.30 (m, 6$H_{\text{both rotamers}}$), 0.97 – 0.85 (m, 3$H_{\text{both rotamers}}$).

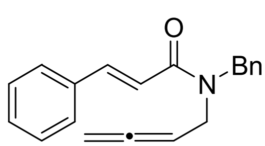
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.19, 143.39, 135.30, 129.70, 128.83, 127.86, 117.65, 117.05, 82.79, 79.32, 72.77, 71.57, 47.50, 47.17, 40.91, 37.83, 35.18, 33.86, 31.49, 29.16, 28.48, 27.67, 26.47, 23.87, 22.57, 20.82, 20.59, 17.50, 17.30, 14.65, 14.00, 7.93.



***N*-(buta-2,3-dienyl)-*N*-hexylcinnamamide (1a)** The general procedure A was followed using propargyl amide **S6** (50 mg, 0.19 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/1) afforded **1a** (38.9 mg, 0.13 mmol) as a brown oil in a 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 15.3, 11.1 Hz, 1H), 7.52 (d, *J* = 6.3 Hz, 2H), 7.37 (d, *J* = 4.9 Hz, 3H), 6.84 (dd, *J* = 15.4, 6.1 Hz, 1H), 5.30 – 5.14 (m, 1H), 4.93 – 4.76 (m, 2H), 4.11 – 4.01 (m, 2H), 3.48 – 3.39 (m, 2H), 1.74 – 1.50 (m, 4H), 1.38-1.25 (m, 6H), 0.97 – 0.82 (m, 6H).

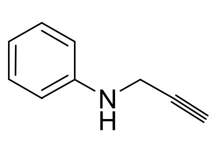
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.33, 208.65, 166.52, 166.21, 142.75, 142.36, 135.45, 129.56, 129.48, 128.79, 128.31, 127.80, 126.85, 118.06, 117.51, 87.84, 86.88, 77.82, 76.11, 47.69, 47.15, 46.70, 45.40, 40.91, 31.66, 31.50, 29.44, 27.88, 26.75, 26.55, 23.87, 22.59, 20.82, 17.51, 17.31, 14.66, 14.05, 14.00.



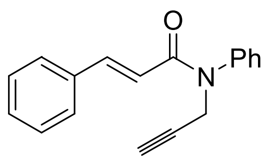
***N*-benzyl-*N*-(buta-2,3-dienyl)cinnamamide (1b)** The general procedure B was followed using cinnamic acid (300 mg, 2.03 mmol) and **S4**. Purification by silica gel column chromatography (PE/Et_2O = 1/1) afforded **1b** (476.8 mg, 1.65 mmol) as a pale yellow oil in a 81% yield as a mixture of rotamers (56:44).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.74 (m, 1$H_{\text{both rotamers}}$), 7.58-7.51 (m, 1$H_{\text{both rotamers}}$), 7.47-7.42 (m, 1$H_{\text{both rotamers}}$), 7.40-7.25 (m, 8$H_{\text{both rotamers}}$), 6.91 (d, *J* = 15.4 Hz, 1H_{major}), 6.82 (d, *J* = 15.4 Hz, 1H_{minor}), 5.30 – 5.18 (m, 1H_{minor}), 5.18 – 5.07 (m, 1H_{major}), 4.90 – 4.76 (m, 2$H_{\text{both rotamers}}$), 4.71 (d, *J* = 9.8 Hz, 2$H_{\text{both rotamers}}$), 4.14-4.09 (m, 2H_{minor}), 4.04 – 3.93 (m, 2H_{major}).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.55, 208.73, 166.89, 143.50, 143.14, 137.55, 136.99, 135.39, 135.22, 129.66, 128.94, 128.81, 128.66, 128.59, 128.43, 128.36, 128.04, 127.87, 127.68, 127.43, 126.84, 126.65, 126.37, 117.62, 117.43, 87.26, 86.38, 77.80, 76.24, 50.54, 49.38, 45.64, 45.02.



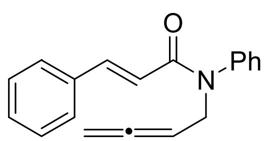
***N*-(prop-2-ynyl)benzenamine (S9)** To a stirred solution of aniline (938 mg, 10.08 mmol) in DMF (10 mL) potassium carbonate (695.8 mg, 5.04 mmol) and propargyl-bromide (80% solution in toluene) (239 µL, 2.52 mmol) were added. The reaction mixture was stirred overnight at room temperature. Reaction mixture was thereafter diluted with diethyl-ether (30 mL) and washed with water (4 x 20 mL). The organic phase was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Crude oil was purified by silica gel column chromatography (PE/Et_2O = 1/3) to afford **S9** in 52 % yield as a yellow oil (171.7 mg, 1.31 mmol). The spectral data are consistent with those reported in the literature.[5]



***N*-phenyl-*N*-(prop-2-ynyl)cinnamamide (S10)** The general procedure B was followed using cinnamic acid (161 mg, 1.09 mmol) and **S9** (171.0 mg, 1.30 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/1) afforded **S10** (173.5 mg, 0.66 mmol) as a brown oil in a 61% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 15.5 Hz, 1H), 7.45 (dt, *J* = 6.9, 4.4 Hz, 3H), 7.35 – 7.27 (m, 7H), 6.30 (d, *J* = 15.5 Hz, 1H), 4.61 (d, *J* = 2.4 Hz, 2H), 2.23 (t, *J* = 2.3 Hz, 1H).

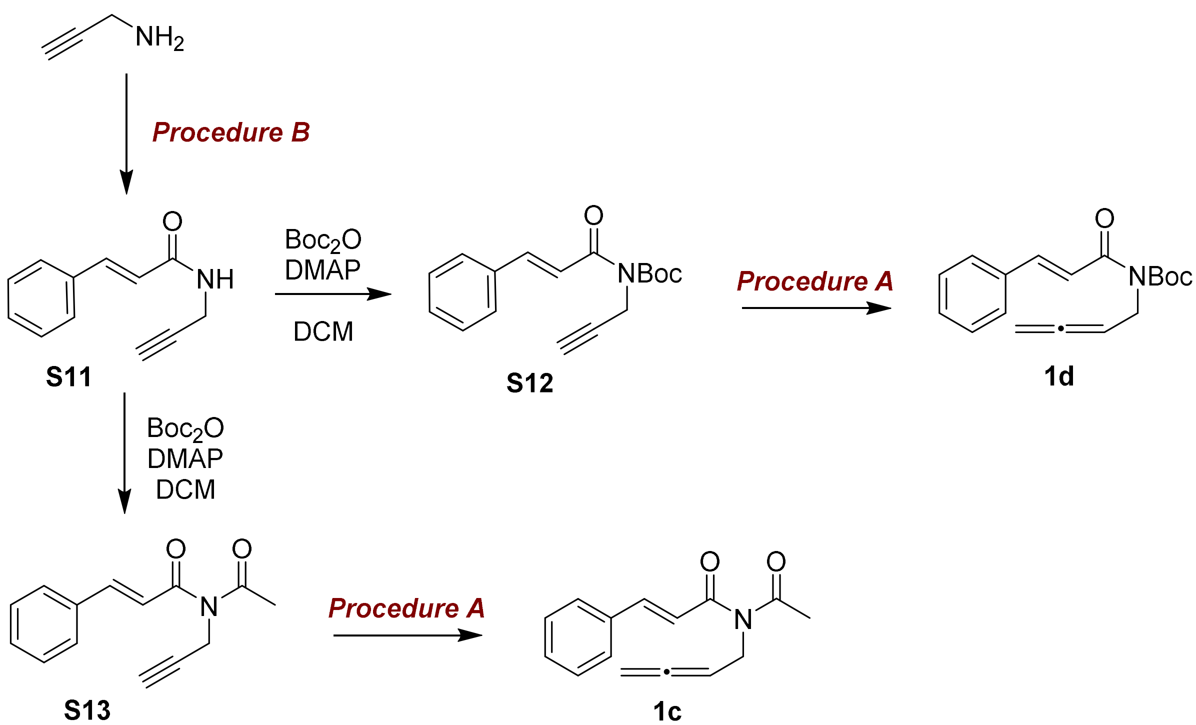
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.71, 142.89, 141.44, 135.03, 129.71, 129.66, 128.70, 128.33, 128.31, 127.94, 118.17, 85.41, 82.84, 79.09, 72.13, 38.82.



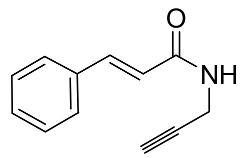
***N*-(buta-2,3-dienyl)-*N*-phenylcinnamamide (1e)** The general procedure A was followed using propargyl amide **S9** (150 mg, 0.57 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/1) afforded **1e** (91.2 mg, 0.35 mmol) as a yellow oil in a 62% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 15.5 Hz, 1H), 7.46 – 7.22 (m, 10H), 6.32 (d, *J* = 15.5 Hz, 1H), 5.30 (p, *J* = 6.6 Hz, 1H), 4.75 – 4.67 (m, 2H), 4.47 – 4.41 (m, 2H).

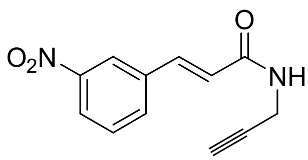
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.44, 165.75, 142.12, 142.08, 135.19, 129.54, 129.49, 128.67, 128.29, 127.87, 127.79, 118.85, 86.55, 76.27, 48.68.



Scheme 3s



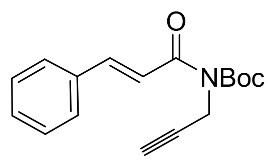
***N*-(prop-2-ynyl)cinnamamide (S11)** The general procedure B was followed using cinnamic acid (250 mg, 1.69 mmol) and propargyl amine (153.4 µL, 1.86 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/3) afforded **S11** (256.6 mg, 1.39 mmol) as a brown oil in a 82% yield.[6]



(*E*)-3-(3-nitrophenyl)-*N*-(prop-2-ynyl)acrylamide (S11b) The general procedure B was followed using *m*-nitrocinnamic acid (520 mg, 2.69 mmol) and propargyl amine (188.0 µL, 2.96 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/3) afforded **S11b** (420.6 mg, 1.83 mmol) as a brown oil in a 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 15.6 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 6.52 (d, *J* = 15.6 Hz, 1H), 5.84 (s, 1H), 4.22 (dd, *J* = 5.2, 2.5 Hz, 2H), 2.29 (s, 1H).

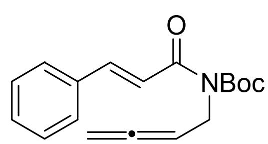
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.39, 164.20, 139.43, 136.38, 133.97, 129.98, 124.22, 122.66, 121.81, 79.04, 72.12, 29.62.



(*E*)-tert-butyl cinnamoyl(prop-2-ynyl)carbamate (S12) To a stirred solution of **S11** (150 mg, 0.82 mmol) in anhydrous dichloromethane (10 mL), under nitrogen atmosphere, Boc_2O (353.5 mg, 1.62 mmol), DMAP (90.8 mg, 0.81 mmol) and Et_3N (112.8 µL, 0.81 mmol) were added. The mixture was thereafter stirred overnight at room temperature. Upon completion the reaction mixture was concentrated under reduced pressure. Crude oil was purified by silica gel column chromatography (PE/Et_2O = 2/1) to afford **S12** (208.2 mg, 0.5986 mmol) as a white amorphous solid in a 73 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 15.6 Hz, 1H), 7.63 – 7.50 (m, 3H), 7.37 (dd, *J* = 5.0, 1.8 Hz, 3H), 4.54 (d, *J* = 2.3 Hz, 2H), 2.17 (t, *J* = 2.3 Hz, 1H), 1.58 (s, 9H).

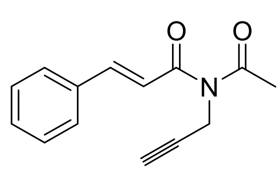
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.82, 152.31, 144.20, 135.04, 130.09, 128.81, 128.26, 120.78, 84.01, 79.60, 70.28, 34.08, 28.07.



(*E*)-tert-butyl buta-2,3-dienyl(cinnamoyl)carbamate (1d) The general procedure A was followed using the correspondent propargyl amide (100 mg, 0.54 mmol). Purification by silica gel column chromatography (PE/Et_2O = 2/1) afforded **1d** (111.4 mg, 0.37 mmol) as a white amorphous solid in a 69% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 15.6 Hz, 1H), 7.58-7.53 (m, 2H), 7.50 (d, *J* = 15.6 Hz, 1H), 7.40 – 7.33 (m, 3H), 5.26 (p, *J* = 6.4 Hz, 1H), 4.84 – 4.73 (m, 2H), 4.37 (dt, *J* = 5.9, 2.8 Hz, 2H), 1.55 (s, 9H).

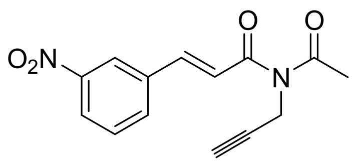
^{13}C NMR (101 MHz, $CDCl_3$) δ 208.84, 168.43, 153.05, 143.33, 135.19, 129.91, 128.77, 128.19, 121.35, 87.45, 83.20, 76.81, 43.09, 28.10.



***N*-acetyl-*N*-(prop-2-ynyl)cinnamamide (S13)** To a stirred solution of **S11** (300 mg, 1.62 mmol) in anhydrous dichloromethane (10 mL), under nitrogen atmosphere, Ac_2O (306.3 µL, 3.24 mmol), DMAP (181.6 mg, 1.62 mmol) and Et_3N (225.6 µL, 1.62 mmol) were added. The mixture was thereafter stirred overnight at room temperature. Upon completion the reaction mixture was concentrated under reduced pressure. Crude oil was purified by silica gel column chromatography (PE/Et_2O = 1/1) to afford **S13** (205.9 mg, 0.91 mmol) as a white amorphous solid in a 56 % yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 15.5 Hz, 1H), 7.58 (s, 2H), 7.41 (s, 3H), 7.21 (d, *J* = 15.5 Hz, 1H), 4.57 (s, 2H), 2.54 (s, 3H), 2.31 (d, *J* = 1.1 Hz, 1H).

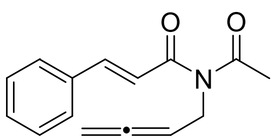
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.48, 168.28, 146.08, 134.50, 130.69, 128.98, 128.45, 119.57, 78.82, 72.14, 33.85, 26.10.



(*E*)-N-acetyl-3-(3-nitrophenyl)-N-(prop-2-ynyl)acrylamide (S13b) The same procedure as for the synthesis of **S13b** was used. Starting from (230 mg, 1 mmol) of **S11b,** 80 mg of **S13b** was afforded in a 29% yield as a pale yellow oil. Silica gel column chromatograhy was used for purification of the crude product (PE/Et_2O = 1/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.79 (d, *J* = 15.5 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 15.5 Hz, 1H), 4.60 (d, *J* = 2.3 Hz, 2H), 2.55 (s, 3H), 2.34 (t, *J* = 2.3 Hz, 1H).

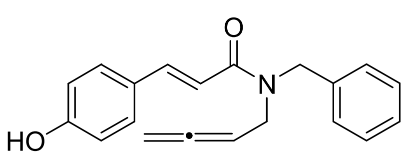
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.54, 167.47, 148.74, 142.16, 136.39, 133.89, 130.00, 124.68, 123.24, 122.67, 78.46, 72.49, 34.03, 25.79.



***N*-acetyl-*N*-(buta-2,3-dienyl)cinnamamide (1c)** The general procedure A was followed using propargyl amide **S13** (100 mg, 0.38 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/1) afforded **1c** (63.19 mg, 0.26 mmol) as a yellow amorphous solid in a 69% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 15.5 Hz, 1H), 7.56 (dd, *J* = 6.1, 2.9 Hz, 2H), 7.43 – 7.37 (m, 3H), 7.11 (d, *J* = 15.5 Hz, 1H), 5.31 (p, *J* = 6.1 Hz, 1H), 4.89 (dt, *J* = 6.4, 3.1 Hz, 2H), 4.40 (dt, *J* = 6.0, 3.1 Hz, 2H), 2.49 (s, 3H).

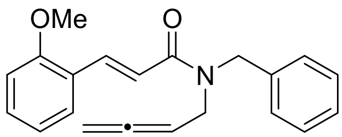
^{13}C NMR (101 MHz, $CDCl_3$) δ 208.56, 173.24, 168.93, 145.22, 134.69, 130.47, 128.94, 128.30, 120.12, 87.54, 78.00, 42.75, 26.17.



(*E*)-*N*-benzyl-*N*-(buta-2,3-dienyl)-3-(4-hydroxyphenyl)acrylamide (1f) The general procedure A was followed using 4-hydroxycinnamic acid (60 mg, 0.37 mmol) and **S4** (56.4 mg, 0.44 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/2) afforded **1f** (97.6 mg, 0.32 mmol) as a yellow oil in a 86% yield as a mixture of rotamers (56:44).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 15.3 Hz, $1H_{both\ rotamers}$), 7.41-7.2 (m, $8H_{both\ rotamers}$), 6.87 (d, *J* = 8.4 Hz, $1H_{major}$), 6.82 (d, *J* = 8.3 Hz, $1H_{minor}$), 6.74 (d, *J* = 15.4 Hz, $1H_{major}$), 6.66 (d, *J* = 15.3 Hz, $1H_{minor}$), 5.28 – 5.17 (m, $1H_{minor}$), 5.16 – 5.07 (m, $1H_{major}$), 4.89 – 4.81 (m, $2H_{major}$), 4.80 – 4.75 (m, $2H_{minor}$), 4.71 (d, *J* = 13.0 Hz, $2H_{both\ rotamers}$), 4.16 – 4.05 (m, $2H_{minor}$), 4.05-3.93 (m, $2H_{major}$).

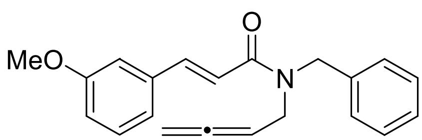
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.53, 208.75, 167.87, 158.40, 144.14, 143.76, 137.31, 136.77, 129.73, 128.97, 128.62, 128.35, 127.97, 127.73, 127.48, 127.25, 126.66, 116.01, 115.35, 114.11, 113.87, 87.07, 86.28, 82.93, 77.84, 76.38, 50.67, 49.53, 45.77, 45.19, 40.88, 33.85, 28.46, 23.85, 22.62, 20.81, 17.50, 17.30, 14.65, 7.92.



(*E*)-*N*-benzyl-*N*-(buta-2,3-dienyl)-3-(2-methoxyphenyl)acrylamide (1g) The general procedure A was followed using 2-methoxycinnamic acid (66 mg, 0.37 mmol) and **S4** (74,4 mg, 0.44 mmol) Purification by silica gel column chromatography (PE/Et_2O = 1/1) afforded **1g** (76.7 mg, 0.24 mmol) as a yellow oil in a 65% yield as a mixture of rotamers (44:56).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.95 (m, $1H_{both\ rotamers}$), 7.50 (d, *J* = 7.5 Hz, $1H_{major}$), 7.41 – 7.22 (m, $6H_{both\ rotamers}$), 7.06 – 6.84 (m, $3H_{both\ rotamers}$), 5.30 – 5.19 (m, $1H_{minor}$), 5.18 – 5.08 (m, $1H_{major}$), 4.88 – 4.79 (m, $2H_{major}$), 4.77 (d, *J* = 6.2 Hz, $2H_{minor}$), 4.72 (s, $2H_{major}$), 4.69 (s, $2H_{minor}$), 4.16 – 4.07 (m, $2H_{minor}$), 4.02 – 3.93 (m, $2H_{major}$), 3.87 (s, $3H_{major}$), 3.77 (s, $3H_{minor}$).

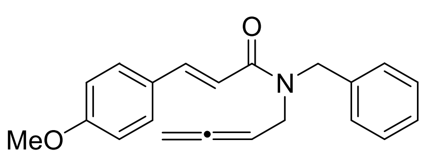
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.57, 208.72, 167.50, 158.30, 139.15, 138.73, 130.73, 129.36, 129.03, 128.84, 128.53, 128.46, 127.34, 126.69, 120.61, 118.45, 111.15, 87.22, 86.47, 82.72, 77.64, 76.13, 55.47, 50.54, 49.22, 45.62, 45.07, 40.91, 23.87, 20.82, 17.50, 17.30, 14.66, 7.93.



(*E*)-*N*-benzyl-*N*-(buta-2,3-dienyl)-3-(3-methoxyphenyl)acrylamide (1h) The general procedure A was followed using 3-methoxycinnamic acid (132 mg, 0.74 mmol) and **S4** (112.6 mg, 0.88 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/1) afforded **1h** (165.2 mg, 0.52 mmol) as a brown oil in a 70% yield as a mixture of rotamers (43:57).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, $1H_{both\ rotamers}$), 7.41 – 7.21 (m, $6H_{both\ rotamers}$), 7.14 (d, *J* = 7.5 Hz, $1H_{major}$), 7.07 – 7.02 (m, $1H_{both\ rotamers}$), 6.98 – 6.85(m, $2H_{both\ rotamers}$), 6.80 (d, *J* = 15.4 Hz, $1H_{minor}$), 5.22 (dd, *J* = 13.1, 6.5 Hz, $1H_{minor}$), 5.16 – 5.07 (m, $1H_{major}$), 4.90 – 4.81 (m, $2H_{major}$), 4.81 – 4.75 (m, $2H_{minor}$), 4.73 – 4.68 (m, $2H_{both\ rotamers}$), 4.17 – 4.04 (m, $2H_{minor}$), 4.03 – 3.94 (m, $2H_{major}$), 3.83 (s, $3H_{major}$), 3.79 (s, $3H_{minor}$).

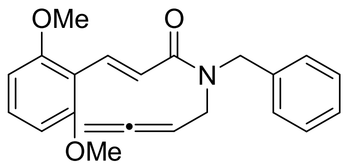
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.55, 208.74, 166.82, 159.88, 143.36, 143.02, 137.53, 136.79, 136.63, 129.81, 128.95, 128.59, 128.43, 127.70, 127.44, 126.65, 120.47, 117.95, 117.78, 115.12, 113.27, 87.25, 86.37, 77.81, 76.26, 55.30, 50.55, 49.37, 45.64, 45.03.



(*E*)-N-benzyl-*N*-(buta-2,3-dienyl)-3-(4-methoxyphenyl)acrylamide (1i) The general procedure A was followed using 4-methoxycinnamic acid (66 mg, 0.37 mmol) and **S4** (56.4 mg, 0.44 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/1) afforded **1i** (93.2 mg, 0.29 mmol) as a yellow in a 79% yield as a mixture of rotamers (54:46).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 15.2 Hz, $1H_{both\ rotamers}$), 7.53 – 7.27 (m, $1H_{both\ rotamers}$), 7.43 – 7.27 (m, $6H_{both\ rotamers}$) 6.88 (dd, *J* = 20.4, 8.3 Hz, $2H_{both\ rotamers}$), 6.78 (d, *J* = 15.4 Hz, $1H_{major}$), 6.69 (d, *J* = 15.2 Hz, $1H_{minor}$), 5.29 – 5.17 (m, $1H_{minor}$), 5.17 – 5.07 (m, $1H_{major}$), 4.84 – 4.72 (m, $2H_{both\ rotamers}$), 4.71 (d, *J* = 10.6 Hz, $2H_{both\ rotamers}$), 4.14 – 4.06 (m, $2H_{minor}$), 4.03 – 3.95 (m, $2H_{major}$) 3.87 – 3.78 (m, $3H_{both\ rotamers}$).

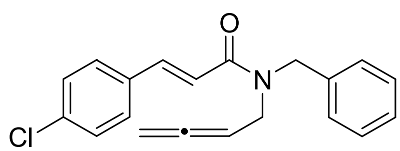
^{13}C NMR (101 MHz, $CDCl_3$) δ 208.75, 167.17, 160.92, 142.85, 129.45, 128.91, 128.56, 128.42, 127.37, 126.66, 115.10, 114.25, 87.29, 86.47, 55.35, 50.49, 49.33, 45.63, 45.01.



(*E*)-*N*-benzyl-*N*-(buta-2,3-dienyl)-3-(2,6-dimethoxyphenyl)acrylamide (1j) The general procedure A was followed using 2,6-dimethoxycinnamic acid (68.6 mg, 0.33 mmol) and **S4** (63.6 mg, 0.40 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/1) afforded **1j** (70.0 mg, 0.20 mmol) as a pale yellow oil in a 60% yield as a mixture of rotamers (52:48).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 15.6, 10.2 Hz, $1H_{both\ rotamers}$), 7.47 – 7.13 (m, $8H_{both\ rotamers}$), 6.55 (d, *J* = 8.3 Hz, $2H_{major}$), 6.49 (d, *J* = 8.3 Hz, $2H_{minor}$), 5.28 – 5,18 (m, $1H_{minor}$), 5.19 – 5.09 (m, $1H_{major}$), 4.86 – 4.79 (m, $2H_{major}$), 4.76 (d, *J* = 6.0 Hz, $2H_{minor}$), 4.72 (s, $2H_{major}$), 4.67 (s, $2H_{minor}$), 4.13 (d, *J* = 5.8 Hz, $2H_{minor}$), 3.97 (s, $2H_{major}$), 3.85 (s, $3H_{both\ rotamers}$), 3.72 (s, $3H_{both\ rotamers}$).

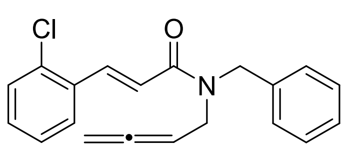
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.56, 208.72, 168.45, 159.74, 133.79, 130.39, 128.71, 128.46, 127.35, 126.75, 120.48, 103.78, 87.23, 55.76, 55.62, 50.52, 49.04, 45.60.



(*E*)-*N*-benzyl-*N*-(buta-2,3-dienyl)-3-(4-chlorophenyl)acrylamide (1k) The general procedure A was followed using 4-chlorocinnamic acid (67 mg, 0.37 mmol) and **S4** (56.4 mg, 0.44 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/1) afforded **1k** (67.8 mg, 0.21 mmol) as a yellow oil in a 56% yield as a mixture of rotamers (43:57).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 15.4, 6.8 Hz, $1H_{both\ rotamers}$), 7.46 (d, *J* = 8.3 Hz, $1H_{both\ rotamers}$), 7.42 – 7.22 (m, $8H_{both\ rotamers}$), 6.87 (d, *J* = 15.4 Hz, $1H_{major}$), 6.78 (d, *J* = 15.4 Hz, $1H_{minor}$), 5.23 (p, *J* = 6.4 Hz, $1H_{minor}$), 5.16 – 5.07 (m, $1H_{major}$), 4.88 – 4.82 (m, $2H_{major}$), 4.82 – 4.75 (m, $2H_{minor}$), 4.72 (s, $1H_{major}$), 4.69 (s, $1H_{minor}$), 4.16 – 4.04 (m, $2H_{minor}$), 4.04 – 3.93 (m, $2H_{major}$).

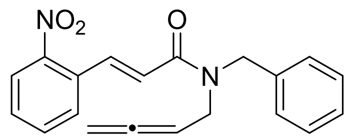
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.53, 208.69, 166.61, 142.12, 141.74, 137.42, 135.48, 133.84, 129.03, 128.60, 128.41, 127.74, 127.48, 126.58, 118.15, 117.94, 87.23, 86.30, 77.88, 76.32, 50.54, 49.41, 45.61, 45.07.



(*E*)-*N*-benzyl-*N*-(buta-2,3-dienyl)-3-(2-chlorophenyl)acrylamide (1l) The general procedure A was followed using 2-chlorocinnamic acid (67 mg, 0.37 mmol) and **S4** (56.4 mg, 0.44 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/1) afforded **1l** (96.9 mg, 0.30 mmol) as a yellow oil in a 81% yield as a mixture of rotamers (52:48).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 15.4 Hz, $1H_{both\ rotamers}$), 7.63 – 7.57 (m, $1H_{major}$), 7.48 – 7.17 (m, $9H_{both\ rotamers}$), 6.90 (d, *J* = 15.5 Hz, $1H_{major}$), 6.81 (d, *J* = 15.4 Hz, $1H_{minor}$), 5.33 – 5.17 (m, $1H_{minor}$), 5.17 – 5.05 (m, $1H_{major}$), 4.89 – 4.83 (m, $2H_{major}$), 4.82 – 4.75 (m, H), 4.72 (s, $2H_{major}$), 4.70 (s, $2H_{minor}$), 4.15 – 4.08 (m, $2H_{minor}$), 4.02 – 3.94 (m, $2H_{major}$).

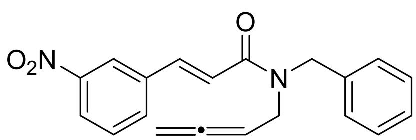
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.58, 208.68, 166.52, 139.36, 138.97, 137.43, 134.78, 133.78, 130.36, 130.21, 128.96, 128.61, 128.50, 127.71, 127.49, 126.90, 126.62, 120.73, 120.53, 87.25, 86.29, 77.98, 76.28, 50.61, 49.35, 45.61, 45.06.



(*E*)-*N*-benzyl-*N*-(buta-2,3-dienyl)-3-(2-nitrophenyl)acrylamide (1m) The general procedure A was followed using 2-nitrocinnamic acid (96.5 mg, 0.5 mmol) and **S4** (96.0 mg, 0.6 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/2) afforded **1m** (106.9 mg, 0.32 mmol) as a yellow oil in a 64% yield as a mixture of rotamers (53:47).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 15.3 Hz, $1H_{both\ rotamers}$), 8.00 (t, *J* = 8.7 Hz, $1H_{both\ rotamers}$), 7.65 – 7.60 (m, $1H_{both\ rotamers}$), 7.58 – 7.43 (m, $2H_{both\ rotamers}$), 7.41 – 7.26 (m, $5H_{both\ rotamers}$), 6.78 (d, *J* = 15.3 Hz, $1H_{major}$), 6.70 (d, *J* = 15.3 Hz, $1H_{minor}$), 5.28 – 5.18 (m, $1H_{minor}$), 5.18 – 5.07 (m, $1H_{major}$), 4.91 – 4.84 (m, $2H_{major}$), 4.82 – 4.77 (m, $2H_{minor}$), 4.72 (s, $2H_{major}$), 4.70 (s, $2H_{minor}$), 4.15 – 4.09 (m, $2H_{minor}$), 4.02 – 3.94 (m, $2H_{major}$).

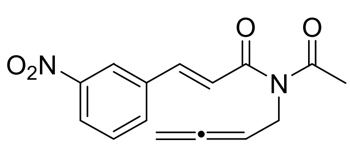
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.58, 208.62, 166.01, 148.39, 138.49, 137.97, 137.21, 136.69, 133.29, 131.71, 129.69, 129.23, 128.98, 128.63, 128.54, 127.76, 127.55, 126.60, 124.80, 123.28, 123.09, 87.25, 86.16, 78.16, 76.39, 50.65, 49.29, 45.53, 44.99.



(*E*)-*N*-benzyl-*N*-(buta-2,3-dienyl)-3-(3-nitrophenyl)acrylamide (1n) The general procedure A was followed using 3-nitrocinnamic acid (77.2 mg, 0.4 mmol) and **S4** (76.8 mg, 0.48 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/2) afforded **1n** (93.5 mg, 0.28 mmol) as a yellow oil in a 70% yield as a mixture of rotamers 40:60.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, $1H_{major}$), 8.27 (s, $1H_{minor}$), 8.24 - 8.15 (m, $1H_{both\ rotamers}$), 7.85 – 7.69 (m, $2H_{both\ rotamers}$), 7.61 – 7.49 (m, $1H_{both\ rotamers}$), 7.42-7.36 (m, $1H_{both\ rotamers}$), 7.35-7.23 (m, XXH), 7.05 (d, *J* = 15.4 Hz, $1H_{major}$), 6.93 (d, *J* = 15.4 Hz, $1H_{minor}$), 5.29 – 5.19 (m, $1H_{minor}$), 5.15-5.09 (m, $1H_{major}$), 4.94 – 4.85 (m, $2H_{major}$), 4.84 – 4.77 (m, $2H_{minor}$), 4.75-4.70 (m, $2H_{both\ rotamers}$), 4.17 – 4.10 (m, $2H_{minor}$), 4.04 – 3.98 (m, $2H_{major}$).

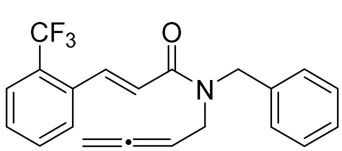
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.55, 208.72, 166.03, 148.72, 140.68, 140.30, 137.20, 137.13, 136.97, 136.68, 134.13, 133.83, 129.92, 129.82, 129.07, 128.67, 128.43, 127.88, 127.60, 126.61, 123.96, 121.92, 121.62, 120.83, 120.61, 87.28, 86.18, 78.07, 50.69, 49.63, 45.80, 45.19.



(*E*)-*N*-acetyl-*N*-(buta-2,3-dienyl)-3-(3-nitrophenyl)acrylamide (1o) The general procedure A was followed using propargyl amide **S13b** (12 mg, 0.04 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/2) afforded **1o** (8 mg, 0.03 mmol) as a yellow oil in a 74% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.24 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 15.5 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 15.9 Hz, 1H), 5.33 (p, *J* = 6.1 Hz, 1H), 4.94 (dt, *J* = 6.4, 3.1 Hz, 2H), 4.41 (dt, *J* = 5.9, 3.1 Hz, 2H), 2.48 (d, *J* = 7.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.51, 173.31, 168.11, 148.70, 141.40, 136.51, 134.06, 129.98, 124.52, 123.64, 122.29, 87.37, 78.25, 42.98, 25.88.

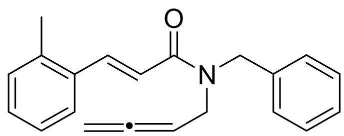


(*E*)-*N*-benzyl-*N*-(buta-2,3-dien-1-yl)-3-(2-(trifluoromethyl)phenyl) acrylamide (1p) The general procedure A was followed using 2-

trifluoromethylcinnamic acid (86.4 mg, 0.40 mmol) and **S4** (61.5 mg, 0.48 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/2) afforded **1p** (57.2 mg, 0.16 mmol) as a yellow oil in a 40% yield as a mixture of rotamers (41:59).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 - 8.05 (m, $1H_{both\ rotamers}$), 7.72 – 7.61 (m, $1H_{both\ rotamers}$ and $1H_{minor}$), 7.55 (t, *J* = 7.4 Hz, $1H_{major}$), 7.51 – 7.23 (m, $7H_{both\ rotamers}$), 6.84 (d, *J* = 15.3 Hz, $1H_{major}$), 6.75 (d, *J* = 15.2 Hz, $1H_{minor}$), 5.23 (dd, *J* = 12.5, 6.1 Hz, $1H_{minor}$), 5.16 – 5.06 (m, $1H_{major}$), 4.87 - 4.75 (m, $2H_{both\ rotamers}$), 4.71 - 4.67 (m, $2H_{both\ rotamers}$), 4.11 (s, $1H_{minor}$), 3.97 (s, $1H_{major}$).

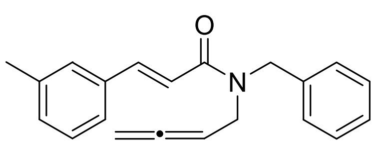
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.58, 208.65, 166.21, 138.87, 138.47, 137.35, 136.77, 134.67, 131.95, 128.96, 128.63, 128.54, 127.93, 127.75, 127.53, 126.62, 126.11, 125.36, 122.54, 87.26, 86.25, 78.03, 76.33, 50.61, 49.35, 45.54, 45.00.



(*E*)-*N*-benzyl-*N*-(buta-2,3-dienyl)-3-o-tolylacrylamide (1q) The general procedure A was followed using (*E*)-3-*o*-tolylacrylic acid (60 mg, 0.37 mmol) and **S4** (56.4 mg, 0.44 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/1) afforded **1q** (90.9 mg, 0.30 mmol) as a brown oil in a 81% yield as a mixture of rotamers (44:56).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, $1H_{both\ rotamers}$), 7.53 (d, *J* = 7.3 Hz, $1H_{major}$), 7.42 – 7.12 (m, $9H_{both\ rotamers}$), 6.81 (d, *J* = 15.3 Hz, $1H_{major}$), 6.72 (d, *J* = 15.3 Hz, $1H_{minor}$), 5.31 – 5.19 (m, $1H_{minor}$), 5.19 – 5.07 (m, $1H_{major}$), 4.87 – 4.82 (m, $2H_{major}$), 4.80 – 4.75 (m, $2H_{minor}$), 4.74 – 4.68 (m, $2H_{both\ rotamers}$), 4.15 – 4.08 (m, $2H_{minor}$), 4.04 – 3.94 (m, $2H_{major}$), 2.46 (s, $3H_{major}$), 2.41 (s, $3H_{minor}$).

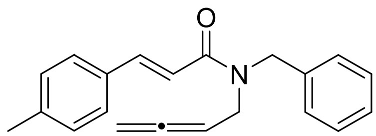
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.56, 208.66, 166.93, 141.26, 140.92, 137.57, 136.97, 134.46, 134.30, 130.75, 129.41, 128.92, 128.65, 128.58, 128.45, 127.66, 127.43, 126.61, 126.15, 118.81, 118.68, 87.28, 86.38, 77.88, 76.22, 50.53, 49.36, 45.59, 45.07.



***(E)*-*N*-benzyl-*N*-(buta-2,3-dienyl)-3-m-tolylacrylamide (1r)** The general procedure A was followed using (*E*)-3-*m*-tolylacrylic acid (63.2 mg, 0.39 mmol) and **S4** (74.4 mg, 0.47 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/1) afforded **1r** (94,5 mg, 0.31 mmol) as a brown oil in a 80% yield as a mixture of rotamers (42:58).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 15.4 Hz, $1H_{both\ rotamers}$), 7.42 – 7.10 (m, $9H_{both\ rotamers}$), 6.89 (d, *J* = 15.4 Hz, $1H_{major}$), 6.82 (d, *J* = 15.4 Hz, $1H_{minor}$), 5.32 – 5.06 (m, $1H_{major}$), 4.90 – 4.81 (m, $2H_{major}$), 4.81 – 4.75 (m, $2H_{minor}$), 4.72 (s, $2H_{major}$), 4.70 (s, $2H_{minor}$), 4.16 – 4.04 (m, $2H_{minor}$), 4.04 – 3.92 (m, $2H_{major}$), 2.37 (s, $3H_{major}$), 2.32 (s, $3H_{minor}$).

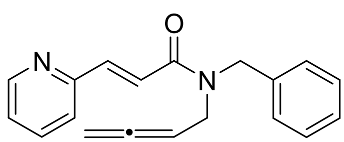
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.49, 208.69, 166.91, 143.69, 143.28, 138.39, 137.54, 136.96, 135.27, 130.49, 128.90, 128.68, 128.56, 128.49, 128.39, 127.65, 127.39, 126.67, 125.05, 117.31, 117.07, 87.27, 86.36, 77.77, 76.24.



(*E*)-*N*-benzyl-*N*-(buta-2,3-dienyl)-3-p-tolylacrylamide (1s) The general procedure A was followed using (*E*)-3-*p*-tolylacrylic acid (42.1 mg, 0.26 mmol) and **S4** (49.6 mg, 0.31 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/1) afforded **1s** (59.1 mg, 0.19 mmol) as a brown oil in a 75% yield as a mixture of rotamers (42:58).

^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 15.3, 4.5 Hz, $1H_{both\ rotamers}$), 7.43 (d, *J* = 7.8 Hz, $2H_{major}$), 7.39 – 7.21 (m, $6H_{both\ rotamers}$), 7.17 (d, *J* = 7.7 Hz, $2H_{major}$), 7.12 (d, *J* = 7.5 Hz, $2H_{minor}$), 6.86 (d, *J* = 15.4 Hz, $1H_{major}$), 6.78 (d, *J* = 15.3 Hz, $1H_{minor}$), 5.26 – 5.18 (m, $1H_{minor}$), 5.16 – 5.06 (m, 1H major), 4.88 – 4.80 (m, $2H_{major}$), 4.80 – 4.74 (m, $2H_{minor}$), 4.72 (s, $2H_{major}$), 4.69 (s, $2H_{minor}$), 4.15 – 4.06 (m, $2H_{minor}$), 4.01 – 3.95 (m, $2H_{major}$), 2.36 (s, $3H_{major}$), 2.32 (s, $3H_{minor}$).

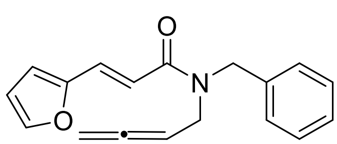
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.48, 208.68, 167.01, 143.49, 143.12, 139.92, 137.58, 137.01, 132.56, 132.39, 129.52, 128.89, 128.54, 128.38, 127.84, 127.62, 127.37, 126.63, 116.43, 116.22, 87.24, 86.39, 77.74, 76.21, 50.45, 49.30, 45.58, 44.95, 21.39.



(*E*)-N-benzyl-*N*-(buta-2,3-dienyl)-3-(pyridin-2-yl)acrylamide (1t) The general procedure A was followed using (E)-3-(pyridin-2-yl)acrylic acid (50.0 mg, 0.33 mmol) and **S4** (64.0 mg, 0.40 mmol). Purification by silica gel column chromatography (EtOAc = 100%) afforded **1t** (66.7 mg, 0.23 mmol) as a brown oil in a 70% yield as a mixture of rotamers (55:45).

^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.1 Hz, $2H_{major}$), 8.57 (d, *J* = 5.0 Hz, $2H_{minor}$), 7.71 – 7.64 (m, $1H_{both\ rotamers}$), 7.42 – 7.22 (m, $7H_{both\ rotamers}$), 7.08 (d, *J* = 15.5 Hz, $1H_{major}$), 6.99 (d, *J* = 15.4 Hz, $1H_{minor}$), 5.23 (p, *J* = 6.5 Hz, $1H_{minor}$), 5.17 – 5.07 (m, $1H_{major}$), 4.91 – 4.83 (m, $2H_{major}$), 4.83 – 4.76 (m, $2H_{minor}$), 4.72 (s, $2H_{major}$), 4.70 (s, $2H_{minor}$), 4.15 – 4.10 (m, $2H_{minor}$), 4.02 – 3.95 (m, $2H_{major}$).

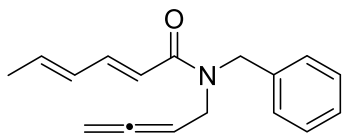
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.49, 208.62, 165.90, 150.48, 150.42, 142.52, 142.32, 140.50, 140.14, 137.13, 136.60, 129.02, 128.63, 128.40, 127.84, 127.56, 126.51, 122.25, 122.05, 121.72, 87.19, 86.11, 78.08, 76.46, 50.59, 49.47, 45.59, 45.12.



(*E*)-N-benzyl-*N*-(buta-2,3-dienyl)-3-(furan-2-yl)acrylamide (1u) The general procedure A was followed using (E)-3-(furan-2-yl)acrylic acid (31 mg, 0.22 mmol) and **S4** (43 mg, 0.27 mmol). Purification by silica gel column chromatography (PE/Et_2O = 1/4) afforded **1u** (38.8 mg, 0.14 mmol) as a yellow oil in a 63% yield as a mixture of rotamers (54:46).

^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 15.1 Hz, $1H_{both\ rotamers}$), 7.44 (s, $1H_{major}$), 7.40 – 7.21 (m, $6H_{both\ rotamers}$), 6.85 – 6.72 (m, $1H_{both\ rotamers}$), 6.55 (dd, *J* = 9.7, 3.0 Hz, $1H_{both\ rotamers}$), 6.44 (d, *J* = 13.6 Hz, $1H_{both\ rotamers}$), 5.27 – 5.16 (m, $1H_{minor}$), 5.16 – 5.06 (m, $1H_{major}$), 4.89 – 4.81 (m, $2H_{major}$), 4.80 – 4.74 (m, $2H_{minor}$), 4.71 (s, $2H_{major}$), 4.68 (s, $2H_{minor}$), 4.12 – 4.05 (m, $2H_{minor}$), 4.00 – 3.92 (m, $2H_{major}$).

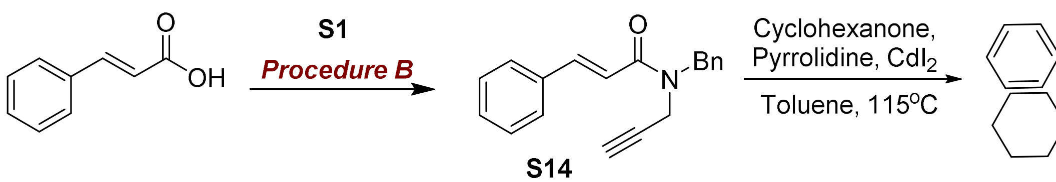
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.46, 208.71, 166.69, 151.75, 151.59, 143.96, 137.55, 136.92, 130.22, 129.87, 128.85, 128.55, 128.35, 127.61, 127.37, 126.74, 115.11, 114.79, 114.05, 113.91, 112.17, 87.25, 86.37, 77.80, 76.25, 50.37, 49.24, 45.53, 44.76.



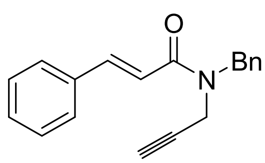
(*2E,4E*)-*N*-benzyl-*N*-(buta-2,3-dienyl)hexa-2,4-dienamide (1v) The general procedure A was followed using (*2E,4E*)-hexa-2,4-dienoic acid (18 mg, 0.16 mmol) and **S4** (30.7 mg, 0.19 mmol). Purification by silica gel column chromatography (PE/Et_2O = 2/1) afforded **1v** (30 mg, 0.12 mmol) as a pale yellow oil in a 75% yield as a mixture of rotamers (45:55).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.17 (m, 6$H_{both\ rotamers}$), 6.35 – 6.02 (m, 3$H_{both\ rotamers}$), 5.18 (dd, *J* = 13.0, 6.5 Hz, 1H_{minor}), 5.05 (dd, *J* = 14.4, 8.4 Hz, 1H_{major}), 4.86 – 4.79 (m, 2H_{major}), 4.78 – 4.72 (m, 2H_{minor}), 4.67 (s, 2H_{major}), 4.60 (s, 2H_{minor}), 4.10 – 4.00 (m, 2H_{minor}), 3.92 - 3.84 (m, 2H_{major}), 1.87 – 1.79 (m, 3$H_{both\ rotamers}$).

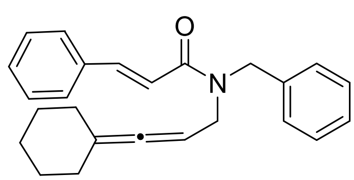
^{13}C NMR (101 MHz, $CDCl_3$) δ 209.49, 208.64, 167.22, 143.93, 143.62, 138.02, 137.87, 137.68, 137.05, 130.26, 128.83, 128.52, 128.38, 127.53, 127.32, 126.58, 118.25, 118.06, 77.68, 76.13, 50.29, 49.04, 45.36, 44.80, 30.33, 18.59.



Scheme 4s



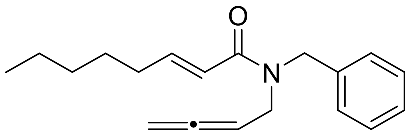
***N*-benzyl-*N*-(prop-2-ynyl)cinnamamide (S14)** The general procedure B was followed using cinnamic acid (100 mg, 0.68 mmol) and **S4** (117.6 mg, 0.81 mmol). Purification by silica gel column chromatography (PE/Et_2O = 2/1) afforded **S4** (148.5 mg, 0.54 mmol) as a white amorphous solid in a 79% which was then used in the next step without further purification.



***N*-benzyl-*N*-(3-cyclohexylideneallyl)cinnamamide (1w)** The substituted allene derivative was synthesised according to the literature procedure, starting from **S14** (117.6 mg, 0.81 mmol).[7] Compound **1w** was obtained in 74% yield as a pale yellow oil as a mixture of rotamers (71:29).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 15.4, 6.1 Hz, 1$H_{both\ rotamers}$), 7.53 (d, *J* = 6.7 Hz, 2H_{major}), 7.44 (d, *J* = 3.8 Hz, 2H_{minor}), 7.41 – 7.28 (m, 7$H_{both\ rotamers}$), 6.89 (d, *J* = 15.4 Hz, 1H_{major}), 6.83 (d, *J* = 15.6 Hz, 1H_{minor}), 5.06 – 5.00 (m, 1H_{minor}), 4.99 – 4.93 (m, 1H_{major}), 4.69 (d, *J* = 5.9 Hz, 2$H_{both\ rotamers}$), 4.06 (d, *J* = 6.2 Hz, 2H_{minor}), 3.92 (d, *J* = 4.7 Hz, 2H_{major}), 2.08 (d, *J* = 5.0 Hz, 4$H_{both\ rotamers}$), 1.60 – 1.48 (m, 6$H_{both\ rotamers}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.67, 166.89, 142.72, 137.85, 135.54, 129.50, 128.90, 128.77, 128.55, 128.37, 127.81, 127.31, 126.66, 117.93, 106.60, 85.36, 49.21, 46.25, 31.42, 27.36, 27.09, 25.92.



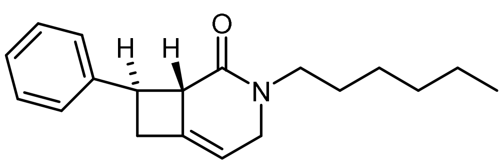
(*E*)-*N*-benzyl-*N*-(buta-2,3-dienyl)oct-2-enamide (1x) The general procedure A was followed using *(E)*-oct-2-enoic acid (71 mg, 0.5 mmol) and **S4** (95.4 mg, 0.6 mmol). Purification by silica gel column chromatography afforded (PE/Et_2O = 2/1) **1x** (113.2 mg, 0.40 mmol) as a pale yellow oil in a 80% yield as as a mixture of rotamers (44:56).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.17 (m, $5H_{both\ rotamers}$), 6.99 (dq, *J* = 14.6, 7.2 Hz, $1H_{both\ rotamers}$), 6.26 – 6.16 (m, $1H_{both\ rotamers}$), 5.24 – 5.13 (m, $1H_{minor}$), 5.06 (dd, *J* = 12.2, 6.0 Hz, $1H_{major}$), 4.87 – 4.80 (m, $2H_{major}$), 4.75 (d, *J* = 6.2 Hz, $2H_{minor}$), 4.65 (s, $2H_{major}$), 4.60 (s, $2H_{minor}$), 4.07 – 3.96 (m, $2H_{minor}$), 3.96 – 3.84 (m, $2H_{major}$), 2.22 (dd, *J* = 13.9, 6.9 Hz, $2H_{major}$), 2.15 (dd, *J* = 14.0, 7.0 Hz, $2H_{minor}$), 1.43 – 1.23 (m, $6H_{both\ rotamers}$), 0.94 – 0.88 (m, $3H_{both\ rotamers}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.55, 208.69, 167.11, 147.83, 147.46, 137.65, 137.04, 128.82, 128.52, 128.42, 127.54, 127.33, 126.64, 120.18, 87.14, 86.41, 77.60, 76.08, 50.36, 48.96, 45.42, 44.73, 40.92, 32.55, 32.49, 31.38, 31.31, 28.48, 28.02, 23.88, 22.46, 20.83, 17.51, 17.30, 14.66, 13.98, 7.93.

General procedure C

To a 1 dram vial equipped with magnetic stir bar were added allene 0.06 mmol, $Ir(ppy)_3$ 1 mol % and DCM (3 mL). The solution was sparged with nitrogen, sealed and irradiated with Blue LED strips (distance from the light source 12 cm) for 18-60 hours at room temperature. Conversion was monitored by TLC. Upon completion the reaction mixture was concentrated under reduced pressure and purified by chromatography on silica gel (mesh 230–400) using petroleum ether and Et_2O.



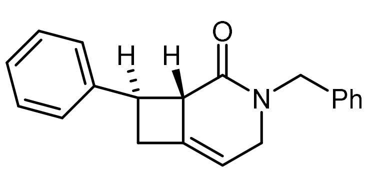
***trans*-3-hexyl-8-phenyl-3-azabicyclo[4.2.0]oct-5-en-2-one (2a)** The general procedure C was followed using **1a** (17.0 mg, 0.06mmol). After 60h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/1) which afforded **2a** (10.2 mg, 0.036 mmol) as a yellow oil in a 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 5.57-5.52 (m, 1H), 4.13-4.05 (m, 1H), 3.76-3.66 (m, 2H), 3.52 (dd, *J* = 14.4, 7.5 Hz, 1H), 3.46-3.40 (m, 1H), 3.35 – 3.28 (m, 1H), 3.09 – 2.96 (m, 2H), 1.61-1.55 (m, 2H), 1.35-1,27 (m, 6H), 0.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.63, 143.26, 138.88, 128.31, 126.85, 126.29, 110.43, 51.96, 49.05, 47.03, 42.72, 35.51, 31.62, 27.42, 26.60, 22.58, 14.03.

IR (v_{max}/cm^{-1}): 2926, 1664, 1220, 1091, 750, 698.

HRMS (ESI) m/z calcd for [$C_{19}H_{25}NO + Na^+$]: 306.18284, found 306.18241.



***trans*-3-benzyl-8-phenyl-3-azabicyclo[4.2.0]oct-5-en-2-one (2b)** The general procedure C was followed using **1b** (17.3 mg, 0.06mmol). After 18h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/1) which afforded **2b** (13.5 mg, 0.047 mmol) as a yellow oil in a 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.20 (m, 8H), 5.48 (s, 1H), 4.66 (dd, *J* = 55.0, 14.7 Hz, 2H), 3.98 (dd, *J* = 16.1, 2.1 Hz, 1H), 3.79 (q, *J* = 8.3 Hz, 1H), 3.67 (dd, *J* = 16.1, 5.9 Hz, 1H), 3.54 (d, *J* = 2.3 Hz, 1H), 3.11 – 2.95 (m, 2H).

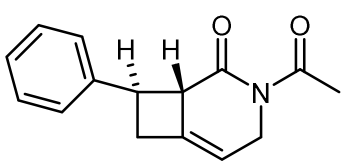
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.94, 143.12, 138.56, 137.18, 128.66, 128.36, 128.04, 127.45, 126.84, 126.37, 110.37, 51.82, 49.94, 48.61, 42.91, 35.74.

IR (v_{max}/cm^{-1}): 3027, 1641, 1446, 1077, 733, 697

HRMS (ESI) m/z calcd for [$C_{20}H_{19}NO + Na^+$]: 312.13588, found 312.13486.

Preparative scale synthesis of cycloadduct 2b

To a borosilicate test tube equipped with a magnetic stir bar were added allene **1b** (145 mg, 0.5 mmol), $Ir(ppy)_3$, (3.3 mg, 1 mol %) and DCM (20 mL). The solution was sparged with nitrogen, sealed with septum and irradiated with Blue LED strips (distance from the light source 12 cm) for 18 hours at room temperature. Upon completion the reaction mixture was concentrated under reduced pressure and purified by chromatography on silica gel (mesh 230–400) (PE/Et_2O = 1/1). Product **2b** was obtained in 76% yield (110 mg, 0.38 mmol) as a yellow oil.



***trans*-3-acetyl-8-phenyl-3-azabicyclo[4.2.0]oct-5-en-2-one (2c)** The general procedure C was followed using **1c** (14.5 mg, 0.06mmol). After 18h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/1) which afforded **2c** (10.4 mg, 0.043 mmol) as colorless triclinic crystals in a 72% yield.

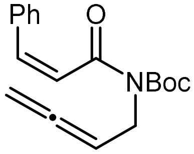
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.26 (m, 5H), 5.73 – 5.56 (m, 1H), 4.83 (dd, *J* = 16.8, 6.2 Hz, 1H), 4.01 – 3.90 (m, 1H), 3.84 (q, *J* = 8.2 Hz, 1H), 3.67 (dd, *J* = 4.6, 1.9 Hz, 1H), 3.17 – 3.02 (m, 2H), 2.59 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.25, 173.15, 142.47, 138.74, 128.57, 126.71, 126.63, 112.12, 53.80, 45.20, 42.17, 35.13, 27.40.

IR (v_{max}/cm^{-1}): 3058, 1954, 1647, 1264, 763, 695.

HRMS (ESI) m/z calcd for [$C_{15}H_{15}NO_2 + Na^+$] 264.09950, found 264.09928.

Melting point 112 – 114 °C



(*Z*)-tert-butyl buta-2,3-dienyl(3-phenylacryloyl)carbamate (3d)

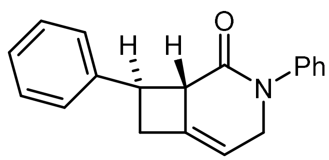
The general procedure C was followed using **1d** (30.0 mg, 0.1mmol). After 60h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/2) which afforded **3d** (23 mg, 0.07 mmol) as a yellow oil in a 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.26 (m, 5H), 6.69 (d, *J* = 12.5 Hz, 1H), 6.41 (d, *J* = 12.5 Hz, 1H), 5.28 – 5.18 (m, 1H), 4.83 – 4.76 (m, 2H), 4.31 (dt, *J* = 5.9, 2.9 Hz, 2H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.82, 168.90, 152.55, 135.40, 134.98, 128.81, 128.35, 128.22, 125.32, 87.13, 83.54, 76.98, 42.18, 27.97.

IR (v_{max}/cm^{-1}): 2978, 1728, 1393, 1146, 1036, 848.

HRMS (ESI) m/z calcd for [$C_{18}H_{21}NO_3$+Na^+]: 322.14136, found 322.14017.



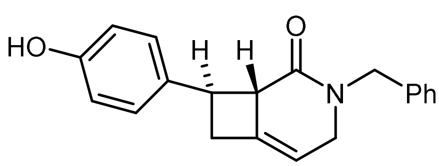
***trans*-3,8-diphenyl-3-azabicyclo[4.2.0]oct-5-en-2-one (2e)** The general procedure C was followed using **1e** (16.5 mg, 0.06mmol). After 60h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/1) which afforded **2e** (11.9 mg, 0.043 mmol) as a yellow oil in a 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.43 – 7.20 (m, 8H), 5.68 (s, 1H), 4.58 – 4.49 (m, 1H), 4.06 (dd, *J* = 15.8, 5.4 Hz, 1H), 3.89 (q, *J* = 8.4 Hz, 1H), 3.64 (dd, *J* = 6.6, 3.9 Hz, 1H), 3.12 (p, *J* = 13.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.11, 143.08, 142.78, 139.37, 129.09, 128.34, 126.84, 126.74, 126.37, 126.17, 111.10, 52.60, 52.53, 42.69, 35.29.

IR (v_{max}/cm^{-1}): 3058, 1659, 1494, 1286, 753, 696.

HRMS (ESI) m/z calcd for [$C_{19}H_{17}NO$+H^+]: 276.13829, found 276.13745.



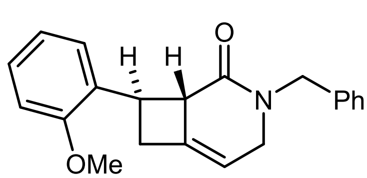
***trans*-3-benzyl-8-(4-hydroxyphenyl)-3-azabicyclo[4.2.0]oct-5-en-2-one (2f)** The general procedure C was followed using **1f** (18.3 mg, 0.06mmol). After 18h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/2) which afforded **2f** (14.64 mg, 0.048 mmol) as a yellow oil in a 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 5H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 5.46 (s, 1H), 4.77 (d, *J* = 14.7 Hz, 1H), 4.55 (d, *J* = 14.7 Hz, 1H), 4.03-3.94 (m, 1H), 3.74 – 3.59 (m, 2H), 3.57-3.50 (m, 1H), 3.05-2.87 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.73, 155.29, 138.67, 136.75, 133.73, 128.73, 128.03, 127.84, 127.57, 115.49, 110.03, 52.11, 50.03, 48.70, 43.00, 36.92.

IR (v_{max}/cm^{-1}): 3272, 2954, 1611, 1433, 1231, 702.

HRMS (ESI) m/z calcd for [$C_{20}H_{19}NO_2$ + H^+]: 306.14886, found 306.14804.



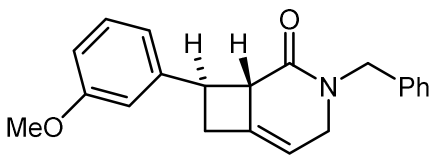
***trans*-3-benzyl-8-(2-methoxyphenyl)-3-azabicyclo[4.2.0]oct-5-en-2-one (2g)** The general procedure C was followed using **1g** (19.1 mg, 0.06mmol). After 18h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/1) which afforded **2g** (16.4 mg, 0.052 mmol) as a yellow oil in a 86% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.4 Hz, 1H), 7.35 – 7.24 (m, 6H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 5.44 (d, *J* = 4.5 Hz, 1H), 4.64 (dd, *J* = 71.1, 14.7 Hz, 2H), 4.00 (d, *J* = 16.1 Hz, 1H), 3.83 – 3.77 (m, 5H), 3.67 (dd, *J* = 16.0, 5.8 Hz, 1H), 3.10 (dd, *J* = 13.4, 6.4 Hz, 1H), 2.90 – 2.80 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.19, 157.63, 139.81, 137.32, 130.86, 128.62, 128.27, 128.06, 127.66, 127.38, 120.64, 110.31, 109.68, 55.27, 49.84, 48.95, 48.68, 40.07, 37.89, 29.71.

IR (v_{max}/cm^{-1}): 2920, 1643, 1492, 1245, 1028, 734.

HRMS (ESI) m/z calcd for [$C_{21}H_{21}NO_2 + H^+$]: 320.16451, found 320.16345.



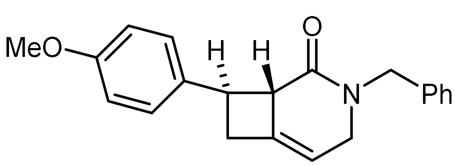
***trans*-3-benzyl-8-(3-methoxyphenyl)-3-azabicyclo[4.2.0]oct-5-en-2-one (2h)** The general procedure C was followed using **1h** (19.1 mg, 0.06mmol). After 18h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/1) which afforded **2h** (16.8 mg, 0.052 mmol) as a yellow oil in a 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.21 (m, 6H), 7.12 – 7.03 (m, 2H), 6.78 (dd, *J* = 8.2, 2.1 Hz, 1H), 5.51 – 5.48 (m, 1H), 4.75 (d, *J* = 14.8 Hz, 1H), 4.56 (d, *J* = 14.8 Hz, 1H), 4.04 – 3.92 (m, 1H), 3.83 (s, 3H), 3.76 (dd, *J* = 16.2, 7.8 Hz, 1H), 3.66 (dd, *J* = 16.2, 5.9 Hz, 1H), 3.57 – 3.50 (m, 1H), 3.10 – 2.95 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.91, 159.74, 144.81, 138.46, 137.14, 129.36, 128.66, 128.00, 127.44, 119.08, 112.38, 112.21, 110.38, 55.26, 51.81, 49.89, 48.58, 42.96, 35.69.

IR (v_{max}/cm^{-1}): 2939, 1661, 1640, 1260, 1042, 733.

HRMS (ESI) m/z calcd for [$C_{21}H_{21}NO_2 + H^+$]: 320.16451, found 320.16428.



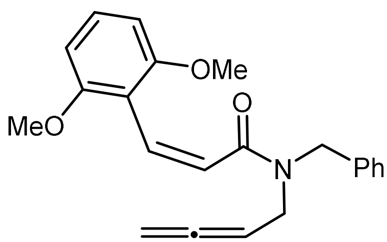
***trans*-3-benzyl-8-(4-methoxyphenyl)-3-azabicyclo[4.2.0]oct-5-en-2-one (2i)** The general procedure C was followed using **1i** (19.1 mg, 0.06mmol). After 18h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/1) which afforded **2i** (16.8 mg, 0.052 mmol) as a yellow oil in a 88% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.36 – 7.24 (m, 5H), 6.88 (d, *J* = 8.5 Hz, 2H), 5.46 (s, 1H), 4.72 (d, *J* = 14.7 Hz, 1H), 4.58 (d, *J* = 14.7 Hz, 1H), 4.02 – 3.93 (m, 1H), 3.80 (s, 3H), 3.75 – 3.62 (m, 2H), 3.52 – 3.44 (m, 1H), 3.00 (dt, *J* = 22.4, 12.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.00, 158.21, 138.60, 137.19, 135.36, 128.64, 128.01, 127.87, 127.42, 113.77, 110.26, 55.31, 52.03, 49.89, 48.60, 42.38, 35.91.

IR (v_{max}/cm^{-1}): 3033, 1643, 1512, 1246, 1031, 732.

HRMS (ESI) m/z calcd for [$C_{21}H_{21}NO_2 + Na^+$]: 342.14645, found 342.14568.



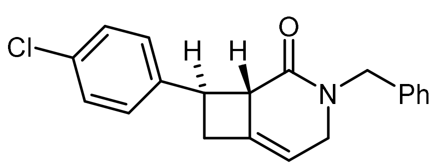
(*Z*)-N-benzyl-3-(2,6-dimethoxyphenyl)-N-(propa-1,2-dienyl)acrylamide (3j) The general procedure C was followed using **1j** (20.1 mg, 0.06mmol). After 18h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/2) which afforded **3j** (18.5 mg, 0.055 mmol) as a yellow oil in a 92% yield.

^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.11 (m, $8H_{both\ rotamers}$), 6.73 (dd, *J* = 12.5, 4.8 Hz, $1H_{both\ rotamers}$), 6.52 (dd, *J* = 8.2, 6.6 Hz, $2H_{both\ rotamers}$), 6.26 (dd, *J* = 12.4, 10.0 Hz, $1H_{both\ rotamers}$), 5.12 (p, *J* = 6.9 Hz, $1H_a$), 4.87 (dt, *J* = 12.6, 6.4 Hz, $1H_b$), 4.79 (dd, *J* = 6.1, 3.1 Hz, 1H), 4.73 – 4.66 (m, $1H_{both\ rotamers}$), 4.55 (d, *J* = 5.4 Hz, $2H_{both\ rotamers}$), 3.94 – 3.87 (m, $2H_{both\ rotamers}$), 3.77 (s, $3H_{both\ rotamers}$), 3.67 (s, $3H_{both\ rotamers}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.79, 209.11, 168.87, 168.61, 157.73, 137.65, 136.97, 129.60, 129.49, 129.13, 128.90, 128.68, 128.58, 128.33, 127.44, 127.24, 127.16, 125.01, 124.56, 113.90, 103.64, 86.60, 86.13, 75.51, 55.65, 55.50, 50.56, 47.05, 45.86, 43.23.

IR (v_{max}/cm^{-1}): 2935, 1954, 1640, 1471, 1108, 730.

HRMS (ESI) m/z calcd for [$C_{22}H_{23}NO_3 + H^+$]: 350.17507, found 350.17387.



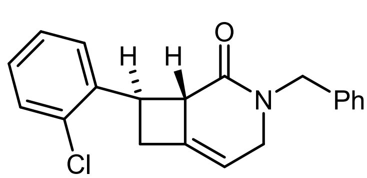
***trans*-3-benzyl-8-(4-chlorophenyl)-3-azabicyclo[4.2.0]oct-5-en-2-one (2k)** The general procedure C was followed using **1k** (19.4 mg, 0.06mmol). After 18h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/1) which afforded **2k** (9.7 mg, 0.03 mmol) as a yellow oil in a 50% yield.

^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.25 (m, 7H), 5.52 – 5.47 (m, 1H), 4.65 (dd, *J* = 59.0, 14.7 Hz, 2H), 4.04 – 3.94 (m, 1H), 3.78 – 3.63 (m, 2H), 3.52 – 3.44 (m, 1H), 3.01 (dt, *J* = 21.1, 12.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.73, 141.58, 138.02, 137.05, 132.15, 128.68, 128.43, 128.30, 128.01, 127.50, 110.61, 51.82, 49.94, 48.60, 42.37, 35.63.

IR (v_{max}/cm^{-1}): 3060, 2846, 1626, 1489, 742, 701.

HRMS (ESI) m/z calcd for [$C_{20}H_{18}ClNO + Na^+$]: 346.09691, found 346.09611.



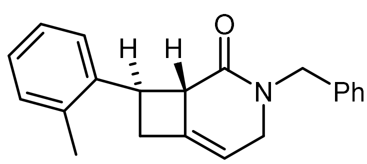
***trans*-3-benzyl-8-(2-chlorophenyl)-3-azabicyclo[4.2.0]oct-5-en-2-one (2l)** The general procedure C was followed using **1l** (19.4mg, 0.06mmol). After 60h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/1) which afforded **2l** (7.56 mg, 0.023 mmol) as a yellow oil in a 39% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.27 (m, 7H), 7.18 (t, *J* = 7.5 Hz, 1H), 5.52 – 5.47 (m, 1H), 4.65 (dd, *J* = 81.7, 14.7 Hz, 2H), 4.02 (d, *J* = 16.1 Hz, 1H), 3.92 (dd, *J* = 16.7, 8.4 Hz, 1H), 3.85 – 3.78 (m, 1H), 3.71 (dd, *J* = 17.2, 5.1 Hz, 1H), 3.32 (dd, *J* = 13.9, 7.6 Hz, 1H), 2.85 – 2.75 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.51, 139.92, 138.33, 137.12, 133.51, 129.45, 128.67, 128.57, 128.10, 127.84, 127.49, 126.95, 110.23, 49.89, 48.68, 48.41, 42.12, 38.33, 29.71.

IR (v_{max}/cm^{-1}): 2920, 1643, 1474, 1235, 1028, 734.

HRMS (ESI) m/z calcd for [$C_{20}H_{18}ClNO + Na^+$]: 346.09691, found 346.09580.



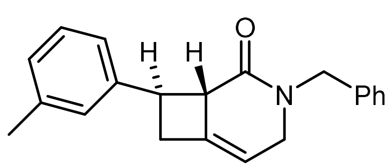
***trans*-3-benzyl-8-(o-tolyl)-3-azabicyclo[4.2.0]oct-5-en-2-one (2q)** The general procedure C was followed using **1q** (18.2 mg, 0.06mmol). After 18h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/1) which afforded **2q** (14.5 mg, 0.048 mmol) as a yellow oil in a 80% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.24 (m, 6H), 7.14 (d, *J* = 4.3 Hz, 2H), 5.48 (s, 1H), 4.65 (dd, *J* = 50.7, 14.7 Hz, 2H), 4.07 – 3.94 (m, 1H), 3.90 – 3.74 (m, 2H), 3.69 (dd, *J* = 17.1, 5.5 Hz, 1H), 3.13 (dd, *J* = 13.8, 7.3 Hz, 1H), 2.87 – 2.76 (m, 1H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.82, 140.61, 138.78, 137.24, 136.03, 130.15, 128.64, 128.09, 127.44, 126.50, 126.27, 126.14, 110.18, 49.91, 49.81, 48.67, 41.49, 37.64, 19.85.

IR (v_{max}/cm^{-1}): 3029, 1644, 1453, 1266, 732, 699.

HRMS (ESI) m/z calcd for [$C_{21}H_{21}NO + Na^+$]: 326.15154, found 326.15066.



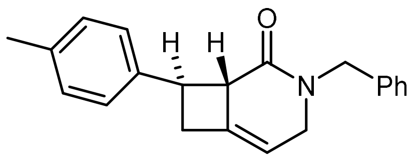
***trans*-3-benzyl-8-(m-tolyl)-3-azabicyclo[4.2.0]oct-5-en-2-one (2r)** The general procedure C was followed using **1r** (18.2 mg, 0.06mmol). After 60h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/1) which afforded **2r** (11.3 mg, 0.037 mmol) as a yellow oil in a 62% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.21 (m, 8H), 7.04 (d, *J* = 7.1 Hz, 1H), 5.50 - 5.45 (m, 1H), 4.75 (d, *J* = 14.7 Hz, 1H), 4.56 (d, *J* = 14.7 Hz, 1H), 3.98 (dd, *J* = 16.1, 2.1 Hz, 1H), 3.75 (q, *J* = 8.3 Hz, 1H), 3.67 (dd, *J* = 16.1, 5.9 Hz, 1H), 3.54 (d, *J* = 2.3 Hz, 1H), 3.11 – 2.94 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.00, 143.08, 138.69, 137.99, 137.20, 128.66, 128.28, 128.03, 127.62, 127.44, 127.16, 123.79, 110.31, 51.80, 49.92, 48.60, 42.88, 35.82, 21.49.

IR (v_{max}/cm^{-1}): 3027, 1643, 1480, 1233, 734, 699.

HRMS (ESI) m/z calcd for [$C_{21}H_{21}NO + Na^+$]: 326.15154, found 326.15118.



***trans*-3-benzyl-8-(p-tolyl)-3-azabicyclo[4.2.0]oct-5-en-2-one (2s)**

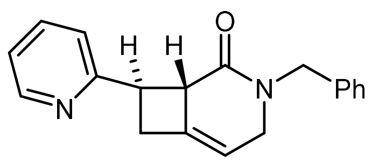
The general procedure C was followed using **1s** (18.2 mg, 0.06mmol). After 60h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/1) which afforded **2s** (10.9 mg, 0.036 mmol) as a yellow oil in a 60% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.25 (m, 7H), 7.16 (d, *J* = 7.9 Hz, 2H), 5.47 (s, 1H), 4.72 (d, *J* = 14.7 Hz, 1H), 4.58 (d, *J* = 14.7 Hz, 1H), 3.98 (dd, *J* = 16.1, 2.1 Hz, 1H), 3.71 (ddd, *J* = 21.8, 16.3, 7.0 Hz, 2H), 3.51 (s, 1H), 3.01 (dt, *J* = 22.5, 12.8 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.02, 140.18, 138.71, 137.22, 135.89, 129.03, 128.66, 128.04, 127.43, 126.73, 110.26, 51.94, 49.93, 48.61, 42.66, 35.82, 21.05.

IR (v_{max}/cm^{-1}): 2921, 1652, 1453, 1170, 734, 699.

HRMS (ESI) m/z calcd for [$C_{21}H_{21}NO$ + Na^+]: 326.15154, found 326.15078.



***trans*-3-benzyl-8-(pyridin-2-yl)-3-azabicyclo[4.2.0]oct-5-en-2-one (2t)**

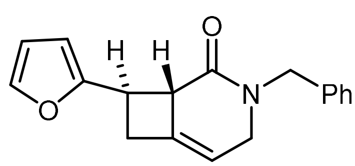
The general procedure C was followed using **1t** (17.4 mg, 0.06mmol). After 18h the reaction mixture was purified by silica gel column chromatography (EtOAc = 100%) which afforded **2t** (7.1 mg, 0.025 mmol) as a yellow oil in a 41% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 2H), 7.44 (d, *J* = 5.0 Hz, 2H), 7.37 – 7.25 (m, 6H), 5.55 – 5.50 (m, 1H), 4.66 (dd, *J* = 59.3, 14.7 Hz, 2H), 4.00 (dd, *J* = 16.3, 2.0 Hz, 1H), 3.82 – 3.65 (m, 2H), 3.56 – 3.50 (m, 1H), 3.06 (dt, *J* = 21.3, 12.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.37, 151.87, 149.72, 137.55, 136.94, 128.72, 128.03, 127.57, 122.22, 111.12, 51.36, 50.00, 48.63, 42.01, 35.00.

IR (v_{max}/cm^{-1}): 3029, 1643, 1599, 1414, 1071, 734.

HRMS (ESI) m/z calcd for [$C_{19}H_{18}N_2O$ + H^+]: 291.14919, found 291.14826.



***trans*-3-benzyl-8-(furan-2-yl)-3-azabicyclo[4.2.0]oct-5-en-2-one (2u)**

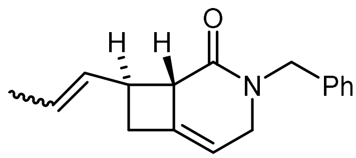
The general procedure C was followed using **1u** (16.7mg, 0.06mmol). After 18h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/3) which afforded **2u** (12.7 mg, 0.046 mmol) as a yellow oil in a 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 6H), 6.34 – 6.29 (m, 1H), 6.21 (d, *J* = 3.1 Hz, 1H), 5.54 – 5.44 (m, 1H), 4.62 (dd, *J* = 42.7, 14.7 Hz, 2H), 3.96 (d, *J* = 15.6 Hz, 1H), 3.75 – 3.61 (m, 3H), 3.15 – 3.04 (m, 1H), 3.00 – 2.91 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.48, 155.55, 141.57, 138.60, 137.14, 128.63, 128.07, 127.45, 111.10, 110.38, 105.67, 50.38, 49.88, 48.58, 36.13, 35.44.

IR (ν_{max}/cm^{-1}): 2917, 2243, 1640, 1479, 727, 699.

HRMS (ESI) m/z calcd for [$C_{18}H_{17}NO_2$ + Na^+]: 302.11515, found 302.11452.



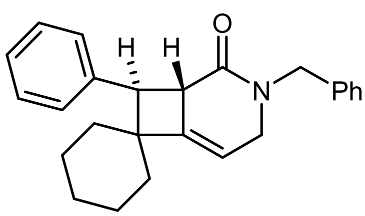
***trans*-3-benzyl-8-(prop-1-en-1-yl)-3-azabicyclo[4.2.0]oct-5-en-2-one (2v)** The general procedure C was followed using **1v** (15.2 mg, 0.06mmol). After 18h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 1/1) which afforded **2v** (12.4 mg, 0.049 mmol) as a yellow oil in a 82% yield as a mixture of isomers.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 5$H_{both\ isomers}$), 5.76 – 5.47 (m, 2$H_{both\ isomers}$), 5.38 (s, 1$H_{both\ isomers}$), 4.70 – 4.50 (m, 2$H_{both\ isomers}$), 3.92 (d, *J* = 16.1 Hz, 1$H_{both\ isomers}$), 3.61 (dd, *J* = 16.0, 5.6 Hz, 1$H_{both\ isomers}$), 3.41 (p, *J* = 8.0 Hz, 1$H_{isomerA}$), 3.25 (s, 1$H_{both\ isomers}$), 3.14 – 3.03 (m, 1$H_{isomerB}$), 2.84 (dd, *J* = 13.7, 7.4 Hz, 1$H_{isomerA\ or\ B}$), 2.75 (dd, *J* = 13.7, 7.4 Hz, 1$H_{isomerA\ or\ B}$), 2.61 (dd, *J* = 21.0, 10.2 Hz, 1$H_{both\ isomers}$), 1.72 (dd, *J* = 8.6, 6.3 Hz, 3$H_{both\ isomers}$).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.12, 170.03, 139.74, 139.22, 137.28, 133.16, 133.02, 128.61, 128.04, 128.00, 127.38, 125.79, 125.73, 109.94, 109.82, 51.47, 50.75, 49.81, 49.78, 48.61, 48.53, 41.28, 36.75, 36.48, 35.79, 17.79, 13.40.

IR (ν_{max}/cm^{-1}): 2915, 1644, 1453, 1233, 732, 699.

HRMS (ESI) m/z calcd for [$C_{17}H_{19}NO$ + H^+]: 254.15394, found 254.15347.



***trans*-3-benzyl-8-phenyl-3-azaspiro[bicyclo[4.2.0]octane-7,1'-cyclohexan]-5-en-2-one (2w)** The general procedure C was followed using **1w** (21.4 mg, 0.06mmol). After 18h the reaction mixture was purified by silica gel column chromatography (PE/Et_2O = 2/1) which afforded **2w** (19.1 mg, 0.053 mmol) as a yellow oil in a 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.19 (m, 9H), 5.72 – 5.62 (m, 1H), 4.65 (s, 2H), 4.08 – 3.98 (m, 1H), 3.80 (td, *J* = 6.2, 3.0 Hz, 1H), 3.69 (ddd, *J* = 16.1, 5.9, 2.3 Hz, 1H), 3.40 (d, *J* = 9.1 Hz, 1H), 1.92 (d, *J* = 14.0 Hz, 1H), 1.66 (ddd, *J* = 21.1, 12.7, 6.0 Hz, 3H), 1.48 (ddd, *J* = 13.3, 10.4, 6.4 Hz, 3H), 1.32 – 1.20 (m, 1H), 1.17 – 1.05 (m, 1H), 0.98 (td, *J* = 12.8, 3.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.72, 147.97, 138.58, 137.32, 128.62, 128.12, 128.09, 127.77, 127.39, 126.34, 109.81, 53.93, 53.36, 49.89, 48.89, 43.52, 38.15, 30.73, 25.86, 24.73, 23.58.

IR (ν_{max}/cm^{-1}): 2925, 1645, 1447, 909, 728, 698.

HRMS (ESI) m/z calcd for [$C_{25}H_{27}NO$ + Na^+]: 380.19849, found 380.19742.

Cyclic voltammetry of compound 1a

The electrochemical properties of **1a** were investigated using cyclic voltammetry (CV) at room temperature. The measurements were performed in a solvent mixture of acetonitrile and dichloromethane (2:1 v/v) with tetrabutylammonium hexafluorophosphate ($n$$Bu_4NPF_6$) (0.1 M) as the supporting electrolyte (98%, Sigma-Aldrich) at 100 mV/s. Prior to recording each voltammogram, the sample was extensively purged with argon.

The CV measurements were carried out using a METROHM Autolab PGSTAT128N electrochemical workstation. A glassy carbon electrode was used as the working electrode, Ag/AgCl served as the reference electrode, and a platinum sheet electrode acted as the counter electrode.

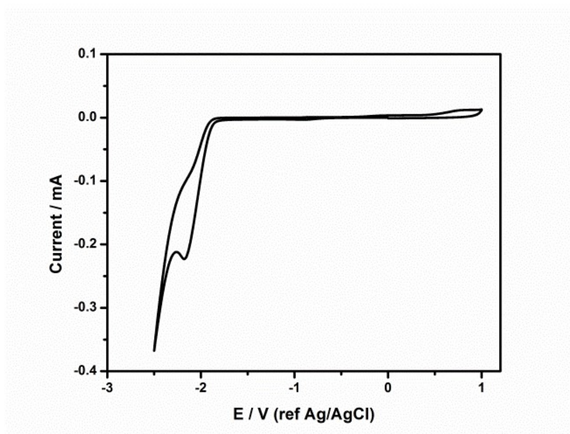


Figure 2S. Cyclic voltammogram of compound **1a**

Crystal structure determination of 2c

Diffraction experiment was performed with Oxford Diffraction Gemini S diffractometer equipped with a Sapphire CCD detector. Data were collected at room temperature. *CrysAlisPro*[8] was used for instrument control and data reduction. Crystal structure was solved with *SHELXT*[9] and refined with *SHELXL*.[10] The *ShelXle*[11] was employed as the interface for refinement procedures. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in idealized positions and refined using a riding model.

Crystal structure model was validated internally through *PLATON*[12] and externally against *Mogul* knowledge base[13] using *Mercury CSD*.[14] Crystallographic data associated with this publication are deposited with the Cambridge Crystallographic Data Centre under the CCDC Number 2233308. They are available for free at https://www.ccdc.cam.ac.uk/structures. Selected crystallographic and refinement details are presented in Table 1S. Molecular packing is depicted in Figure 3S.

Table 1S. Selected crystallographic and refinement details of **2c**

Parameter	**Value**
CCDC number	2233308
Empirical formula	$C_{15}H_{15}NO_2$
Formula weight	241.28
Temperature, K	295(2)
Crystal system	triclinic
Space group	$P\overline{1}$
a / Å	6.17145(16)
b / Å	9.8923(3)
c / Å	11.4954(4)
α / °	64.793(3)
β / °	80.464(3)
γ / °	81.321(2)
V / Å^3	623.65(4)
Z	2
ρ_{calc} / g cm^{-3}	1.285
μ / mm^{-1}	0.085
F(000)	256
Crystal size / mm^3	0.45, 0.48, 0.98
Crystal color	colorless
Crystal shape	block
Wavelength, Å	0.71073
2ϑ range, °	4.6–58.4
Reflections collected	24227
Independent reflections	3138
R_{int}	0.021
R_{sigma}	0.012
Completeness, %	99.9
Reflections used in refinement	3138
Restraints	0
Parameters	164
Goodness-of-fit on F^2	1.059
R_1 [$I \geq 2\sigma(I)$]	0.0547
wR_2 [$I \geq 2\sigma(I)$]	0.1450
R_1 [all data]	0.0666
wR_2 [all data]	0.1550
Largest peak, eÅ^{-3}	0.44
Largest hole, eÅ^{-3}	−0.19

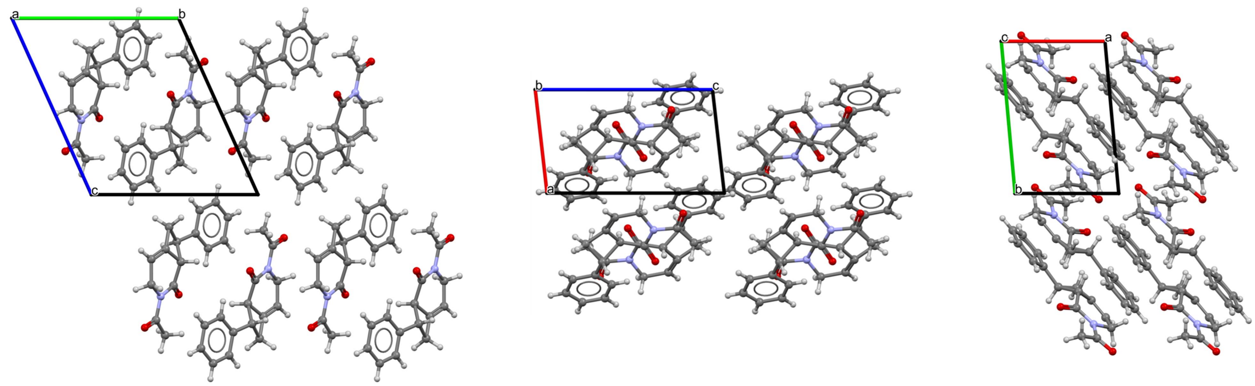


Figure 3S. Crystal structure of **2c** viewed along all three unit cell directions

Computational details

All results are obtained through Gaussian 09 [15] electronic structure program suite (Revision A.03), by using Density Functional Theory (DFT) [16] approach. All calculations have been carried out on B3LYP[17,18] density functional approximation, coupled with 6-311++G[19] orbital basis set, for all atoms except Ir, with the dispersion correction on the D3BJ-level.[20] For the Ir(III) atom, LANL2DZ effective core potential has been used.[21-23] Furthermore, to make calculations as realistic as possible, the solvation effects of DCM have been included using the polarizable conductor continuum model (C-PCM) through the solvent cavity reaction field (SCRF) method.[24] Mentioned computational conditions were applied for full relaxation and optimization of all molecular species of interest. Vibration frequency calculations were conducted at the same level, in order to validate the transition states, and provide the thermodynamic corrections to the energy. All transition states were confirmed to be the saddle points by the presence of single imaginary frequency, belonging to the reaction coordinate. On the other hand, each minimum has zero imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were performed for all transition states in order to trace the reaction pathway and validate the reactants and products.[25,26]

Table 2S. Theoretical values of HOMO-LUMO gap ($E_{(LUMO-HOMO)}$), together with the triplet state energy (E_T) of all critical molecular species, based on relative Gibbs free energy, calculated on B3LYP-D3 level of theory

Calculated theoretical parameters (energies) on B3LYP-D3 level of theory		
Molecular species	**$E_{(LUMO-HOMO)}$** (eV)	***E_T*** (kcal/mol)
$Ir(ppy)_3$	3.6	**54.3**
E conformer:		
1c	4.3	48.1
1o	3.8	48.2
1y	3.9	48.9
Z conformer:		
1c'	5.0	48.0
1o'	3.9	**60.1**
1y'	4.2	48.7

Table 3S. The energy of key molecular species (in atomic units), based on relative Gibbs free energy, calculated on B3LYP-D3 level of theory

Calculated theoretical energies on B3LYP-D3 level of theory in atomic units			
Molecular species	**1c**	**1o**	**1y**
Reactant S_0	-785.867026	-990.44127	-900.404975
Reactant T_1	-785.790423	-990.36448	-900.327115
TS1 S_1	-785.815857	-	-900.354346
TS1 T_1	-785.781667	-	-900.319242
Intermediate S_1	-785.844561	-	-900.380588
Intermediate T_1	-785.845190	-	-900.381478
TS2 S_1	-785.764083	-	-900.371778
TS2 T_1	-785.739001	-	-900.295324
Z- product S_0	-785.856804	-990.433989	-900.396274
Z- product T_1	-785.790423	-990.345532	-900.327115
Final product S_0	-785.888034	-	-900.423000

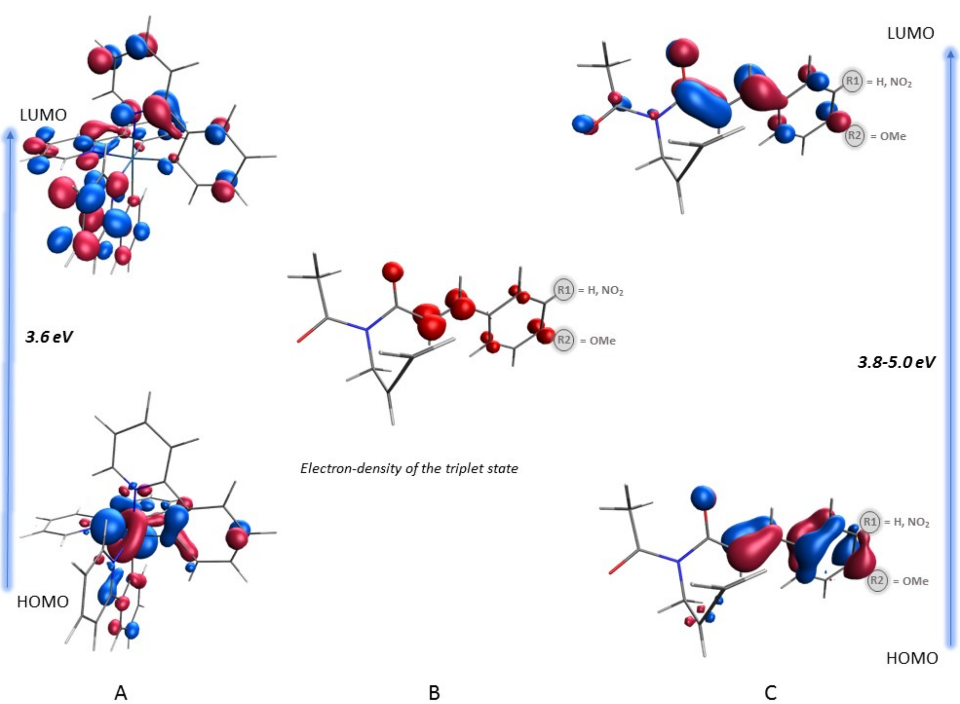


Figure 4S. HOMO and LUMO orbitals and the HOMO-LUMO gap of the Ir(ppy)$_3$ catalyst (A), compounds **1c**, **1o**, **1y** (B), and corresponding spin-electron density of the unrelaxed excited triplet state (C)

Figure 4S shows that the HOMO orbital of the catalyst is obviously one of the *d*-orbitals of the metal ion (d_{z^2}), whereas the LUMO orbital is distributed across the whole ligand compartment (π*(ppy)$_3$) and considerably delocalized. This observation is in accordance with conclusions driven from extensive work done in the field of charge-transfer (CT) properties of Ir^{III}- containing molecular systems.[27–29]

Theoretically obtained results

Herein, the most prominent reaction mechanism was examined within the Density Functional Theory (DFT) [16] framework, by theoretically modeling all terminal molecular species, as well as intermediates and transition states along the specific pathway. The discussion is provided in terms of relative (Gibbs free) energies obtained from quantum-chemical calculations (relative to the ground state of a specific chemical moiety) and presented in Figure 2 in the manuscript.

In regard to the main reaction pathway (thermodynamically more favourable; green path), starting from the excited reactants in their triplet state, calculated barrier is significantly lower (Figure 2) than the barrier for the uncatalyzed reaction, whereby the transition state (TS1) is formed. From this point, the reaction proceeds through a highly exothermic process (~40 kcal/mol), leading to the establishment of the chemical bond and formation of the intermediate molecular species, which also represents the minimal energy (surface) crossing-point between the triplet state and the bi-radical singlet state. The process further proceeds over the singlet bi-radical multideterminantal[30] transition state (TS2), obtained through the Noodleman's methodology,[31,32] called the broken-symmetry (BS). BS approach represents multideterminantal states with an „antiferromagnetically-coupled" Slater determinant, originating from localized bi-radical spin centres. BS orbitals are allowed to relax from the starting form under the action of the variational principle.[33,34] Iso-surface plot of the TS2 electron density (Figure 2) shows that the density is dominantly shared between two carbon atoms which will undergo the formation of the final chemical bond and thus the formation of the final product(s). Calculations revealed that this final step is also exothermic, and that the reaction products are considerably more stable (13.2 and 11.3 kcal/mol for **2c** and **2y**) than the reactants in their initial singlet ground state. All geometries (corresponding coordinates) are provided in below.

Conformational analysis of 1d derivative

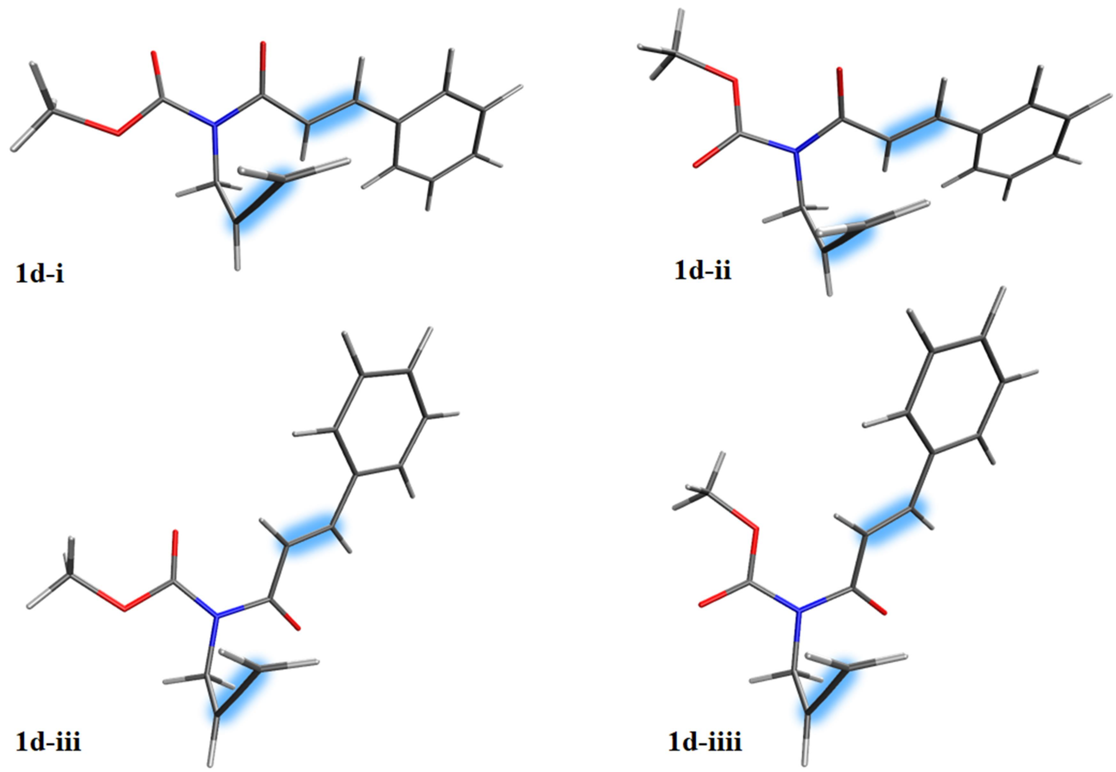


Figure 5S. The most abundant conformers of the molecule **1d*** and the positioning of relevant double bonds.

* *The most abundant structures are obtained using a Python script written for this purpose. Namely, the script used the Z-matrix of the optimized **1d-i** structure, and by determining all rotable bonds, changed the corresponding torsion angle for 120^{o}. All generated structures were relaxed and optimized, using the previously described computational conditions, and all of these structures converged in one of four structures presented in the Figure 5S.*

Table 4S. The energy of 4 most abundant conformers of the molecule **1d** (presented in figure 5S), based on relative Gibbs free energy, and calculated on B3LYP-D3 level of theory

Calculated theoretical energies on B3LYP-D3 level of theory			
Molecular species	**E** (Hartree)	**E difference** (Hartree)	**E difference** (kcal/mol)
1d-i	-861.1060	0.0063	4.0
1d-ii	-861.1071	0.0052	3.3
1d-iii	-861.1123	0.0000	0.0
1d-iiii	-861.1116	0.0007	0.4

In order for the cycloaddition to take place, two double bonds that participate in the reaction should be position in close proximity. In other words, **1d** should adopt either conformation **1d-i** or **1d-ii**. Calculations revealed that these two conformers are less stable than the most stable **1d-iii** (and almost equienergetic **1d-iiii**), most likely due to dipole-dipole interactions or due to electron density interactions of the neighboring O-atoms. All these results suggest that the N-protection should be carefully considered when planning transformations of this type.

Z-conformer geometry investigation

Final important theoretical insight can be extracted from the actual geometry of the Z-conformer(s). In order to determine geometrical differences of two substrates with different reactivity (**1y'** and **1o'**), the corresponding geometrical structures are overlapped and presented in the Figure 6S. The hydrogen atoms are omitted for clarity. Figure 6S clearly shows the pronounced compact arrangement of the **1o'** molecular species. The hypothesis that can be drawn from this insight is that there might be some kind of fine interaction between the allene compartment and π- electrons of the aromatic ring. Detailed examination of possible fine interactions, together with accurate description of complex excited states (and their coupling) requires the utilization of high-level *ab initio* methods. Nevertheless, even with limited (approximative) theoretical tools some important phenomena are detected and some hypothesis and explanations proposed. All of these aspects will be the topic of the future work.

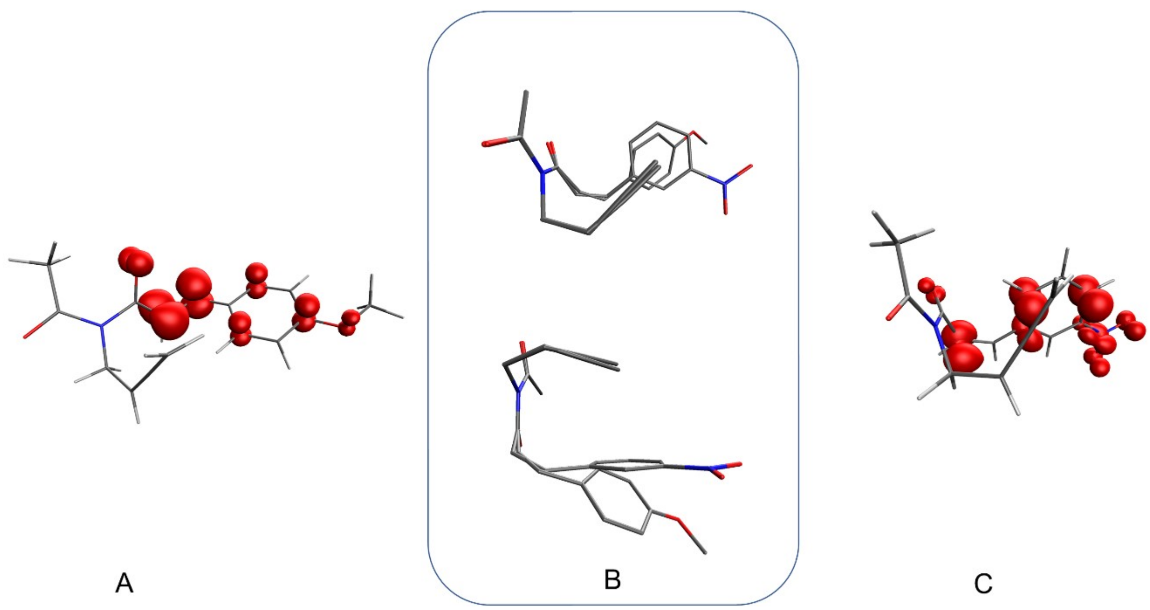


Figure 6S. Z-conformers **1y'** and **1o'** geometry overlap (B) and optimized excited triplet state of **1y'** (A) and **1o'** (C), with visualized corresponding spin-electron density

Optimized geometries for all chemical structures

$Ir(ppy)_3$ S_0

C	-1.221108000	2.615627000	0.590340000
C	-1.182347000	1.266067000	1.076694000
C	-1.974270000	0.975910000	2.216652000
C	-2.753005000	1.963230000	2.847861000
C	-2.771172000	3.287700000	2.353519000
C	-2.004291000	3.609483000	1.223714000
C	-0.391740000	2.892232000	-0.591441000
C	1.107470000	1.923205000	-2.156147000
C	1.272815000	3.139241000	-2.827022000
C	0.575364000	4.269927000	-2.352719000
C	-0.256409000	4.143047000	-1.232374000
H	-1.974770000	-0.033001000	2.620000000
H	-3.346030000	1.706213000	3.723958000
H	-3.373003000	4.049248000	2.843327000
H	-2.019073000	4.628181000	0.844109000
H	1.624122000	1.026662000	-2.475498000
H	1.929958000	3.196773000	-3.688062000
H	0.682936000	5.230800000	-2.847387000
H	-0.794749000	5.004513000	-0.854132000
Ir	0.001026000	-0.001352000	0.029597000
C	-2.310450000	-1.780068000	-0.603811000
C	-2.200322000	-0.001457000	-2.172063000
C	-3.462388000	-2.280802000	-1.248555000
C	-1.664211000	-2.363197000	0.580720000
C	-3.334725000	-0.460875000	-2.848875000
H	-1.673178000	0.889132000	-2.490893000
C	-3.976932000	-1.623601000	-2.373966000
H	-3.949635000	-3.171450000	-0.868984000
C	-2.139197000	-3.538504000	1.209561000
C	-0.515354000	-1.658339000	1.073731000
H	-3.703628000	0.078555000	-3.714590000
H	-4.863098000	-2.005813000	-2.872145000
C	-1.485407000	-4.043529000	2.343436000
H	-3.011530000	-4.060013000	0.823221000
C	0.122607000	-2.200582000	2.218101000
C	-0.349900000	-3.367621000	2.846064000
H	-1.848471000	-4.945505000	2.829939000
H	0.995091000	-1.698516000	2.627077000
H	0.162293000	-3.753860000	3.725696000
C	2.703482000	-1.104565000	-0.594029000
C	1.117209000	-1.911074000	-2.164396000
C	3.720729000	-1.840616000	-1.239252000
C	2.877771000	-0.255785000	0.593161000
C	2.089398000	-2.656362000	-2.839383000
H	0.083014000	-1.909337000	-2.485144000

C	3.417224000	-2.617850000	-2.364683000
H	4.735117000	-1.804137000	-0.859470000
C	1.689342000	0.382913000	1.082151000
C	4.129721000	-0.080388000	1.229127000
H	1.812445000	-3.249066000	-3.704571000
H	4.197297000	-3.185857000	-2.863059000
C	1.833948000	1.206325000	2.227586000
C	4.234044000	0.737513000	2.364139000
H	5.018978000	-0.576799000	0.847632000
C	3.077856000	1.381883000	2.861271000
H	0.960338000	1.709410000	2.633154000
H	5.193874000	0.873648000	2.856344000
H	3.151239000	2.018309000	3.741535000
N	0.296972000	1.799591000	-1.073616000
N	-1.699285000	-0.641762000	-1.084458000
N	1.413310000	-1.153335000	-1.077028000

$Ir(ppy)_3$ T_1

C	-2.723901000	0.950687000	0.605201000
C	-1.741473000	0.033299000	1.098608000
C	-2.091940000	-0.752090000	2.221668000
C	-3.348203000	-0.622876000	2.843515000
C	-4.300702000	0.296534000	2.349043000
C	-3.987293000	1.079955000	1.228289000
C	-2.342176000	1.732377000	-0.581393000
C	-0.601895000	2.125724000	-2.153587000
C	-1.361683000	3.086666000	-2.827048000
C	-2.658915000	3.372996000	-2.351502000
C	-3.147953000	2.694438000	-1.227724000
H	-1.372329000	-1.460267000	2.623698000
H	-3.587336000	-1.232878000	3.712531000
H	-5.269101000	0.395994000	2.832745000
H	-4.722386000	1.784265000	0.847398000
H	0.401322000	1.865721000	-2.467201000
H	-0.948334000	3.595538000	-3.690814000
H	-3.274786000	4.115668000	-2.850066000
H	-4.141633000	2.907606000	-0.851096000
Ir	0.011369000	0.002760000	0.058361000
C	-0.332479000	-2.900475000	-0.589706000
C	-1.642473000	-1.593693000	-2.076486000
C	-0.786423000	-4.080077000	-1.217259000
C	0.586153000	-2.836098000	0.556098000
C	-2.122052000	-2.732362000	-2.731522000
H	-1.949361000	-0.598954000	-2.374027000
C	-1.681352000	-3.998086000	-2.291919000
H	-0.443834000	-5.045823000	-0.864972000
C	1.150025000	-3.988343000	1.150606000
C	0.892491000	-1.524734000	1.045382000

H	-2.817924000	-2.628563000	-3.556797000
H	-2.033838000	-4.902499000	-2.778768000
C	2.025895000	-3.860768000	2.239068000
H	0.912054000	-4.978936000	0.772058000
C	1.787241000	-1.427180000	2.138555000
C	2.343336000	-2.574547000	2.731433000
H	2.458071000	-4.745471000	2.699537000
H	2.036203000	-0.447900000	2.536462000
H	3.022728000	-2.471490000	3.575051000
C	2.640028000	1.208803000	-0.623838000
C	2.098196000	-0.548044000	-2.188575000
C	3.868805000	1.433938000	-1.330827000
C	2.206246000	1.870311000	0.555251000
C	3.290253000	-0.358947000	-2.883928000
H	1.392551000	-1.314280000	-2.492238000
C	4.199524000	0.677686000	-2.440960000
H	4.540158000	2.211958000	-0.979461000
C	0.889411000	1.468308000	1.090941000
C	2.947967000	2.903580000	1.226012000
H	3.523095000	-0.984526000	-3.739361000
H	5.129654000	0.851522000	-2.974574000
C	0.391138000	2.149834000	2.223187000
C	2.416020000	3.527986000	2.351553000
H	3.925763000	3.201421000	0.857132000
C	1.131050000	3.163062000	2.863778000
H	-0.578826000	1.867946000	2.623498000
H	2.986299000	4.308581000	2.852161000
H	0.737193000	3.662412000	3.745582000
N	-1.080768000	1.468412000	-1.067394000
N	-0.767314000	-1.676338000	-1.043094000
N	1.739800000	0.202678000	-1.112904000

1c_Z S_0

C	-0.372259000	1.994182000	-0.617433000
C	-1.099967000	-1.027688000	0.786626000
C	0.359139000	1.725656000	-1.661948000
H	-0.018944000	1.882285000	-2.669188000
H	1.369016000	1.340144000	-1.561804000
C	1.079004000	-0.437869000	1.941909000
H	1.520221000	-0.171543000	2.899389000
C	-0.238288000	-0.680699000	1.956042000
H	-0.763931000	-0.618584000	2.904310000
C	-1.111802000	2.243003000	0.426035000
H	-1.089130000	3.231254000	0.881159000
C	2.021253000	-0.384841000	0.812364000
C	1.952886000	-1.230429000	-0.306208000
C	3.062152000	0.557331000	0.875184000
C	2.884567000	-1.117396000	-1.335109000

H	1.181117000	-1.984364000	-0.360323000
C	3.981418000	0.679589000	-0.161596000
H	3.136168000	1.206101000	1.741459000
C	3.895016000	-0.158708000	-1.273728000
H	2.820538000	-1.783623000	-2.188199000
H	4.767495000	1.423745000	-0.099831000
H	4.615342000	-0.072055000	-2.079267000
C	-2.038598000	1.252473000	1.091328000
H	-3.054893000	1.643251000	1.077949000
H	-1.753946000	1.130628000	2.135037000
N	-2.065085000	-0.069759000	0.444374000
C	-3.022175000	-0.226297000	-0.588571000
O	-3.724934000	0.725273000	-0.880883000
C	-3.174823000	-1.549351000	-1.283550000
H	-2.289971000	-1.772326000	-1.881410000
H	-3.294593000	-2.367121000	-0.572808000
H	-4.049398000	-1.474832000	-1.928905000
O	-0.988146000	-2.095070000	0.208851000

1o_Z S_0

C	-0.693800000	2.078053000	-0.064626000
C	-2.216865000	-1.158732000	0.711586000
C	0.023296000	2.001238000	-1.149735000
H	-0.271416000	2.524729000	-2.055880000
H	0.939914000	1.422239000	-1.185191000
C	0.030214000	-1.162427000	1.877327000
H	0.538607000	-1.204611000	2.836383000
C	-1.305254000	-1.207764000	1.900211000
H	-1.811951000	-1.324382000	2.853753000
C	-1.433711000	2.145774000	1.005143000
H	-1.260336000	2.935735000	1.733119000
C	0.924963000	-1.029639000	0.715864000
C	0.637707000	-1.568827000	-0.548697000
C	2.145464000	-0.369236000	0.897238000
C	1.533112000	-1.434407000	-1.606727000
H	-0.277377000	-2.123120000	-0.700880000
C	3.016811000	-0.238226000	-0.175911000
H	2.408232000	0.045046000	1.860652000
C	2.736338000	-0.760570000	-1.435696000
H	1.293942000	-1.865557000	-2.570974000
H	3.441656000	-0.646694000	-2.246158000
C	-2.577076000	1.215098000	1.330583000
H	-3.511963000	1.776302000	1.326523000
H	-2.449585000	0.812365000	2.333635000
N	-2.730480000	0.096189000	0.385784000
C	-3.429027000	0.387719000	-0.813970000
O	-3.970374000	1.471962000	-0.923372000
C	-3.442032000	-0.617166000	-1.930233000

H	-2.451047000	-1.033921000	-2.109171000
H	-4.105226000	-1.448695000	-1.687536000
H	-3.805399000	-0.106186000	-2.821096000
O	-2.506583000	-2.178995000	0.110861000
N	4.285352000	0.478233000	0.029601000
O	5.027804000	0.627804000	-0.936445000
O	4.541279000	0.895537000	1.155331000

1y_Z S_0

C	1.436106000	1.557783000	-1.548921000
C	1.772371000	-0.897728000	0.547260000
C	0.655332000	2.371295000	-0.894875000
H	1.021043000	3.321700000	-0.514444000
H	-0.386474000	2.126797000	-0.708192000
C	-0.286526000	-2.005966000	-0.475052000
H	-0.561551000	-2.850939000	-1.102146000
C	1.041264000	-1.895385000	-0.263290000
H	1.672364000	-2.633387000	-0.747149000
C	2.223289000	0.731867000	-2.178793000
H	2.317315000	0.793188000	-3.261292000
C	-1.440363000	-1.184804000	-0.117119000
C	-1.446216000	-0.118646000	0.807306000
C	-2.651247000	-1.477103000	-0.768104000
C	-2.593961000	0.614886000	1.043014000
H	-0.549079000	0.120724000	1.356264000
C	-3.812572000	-0.745212000	-0.543849000
H	-2.682069000	-2.295531000	-1.479448000
C	-3.786645000	0.314850000	0.367667000
H	-2.591373000	1.428590000	1.758894000
H	-4.717840000	-1.004759000	-1.075003000
C	3.045052000	-0.352735000	-1.520667000
H	4.095843000	-0.212482000	-1.768484000
H	2.744904000	-1.322744000	-1.915128000
N	2.934939000	-0.370935000	-0.054326000
C	3.920025000	0.346852000	0.653476000
O	4.738950000	1.004787000	0.032861000
C	3.989242000	0.235496000	2.152644000
H	3.274209000	0.921739000	2.609469000
H	3.754494000	-0.766373000	2.509532000
H	4.998722000	0.520121000	2.449366000
O	1.432879000	-0.574873000	1.674476000
O	-4.854276000	1.094736000	0.668564000
C	-6.099708000	0.825822000	0.017239000
H	-6.010818000	0.947630000	-1.066089000
H	-6.455409000	-0.181984000	0.249843000
H	-6.801939000	1.559424000	0.409458000

1c_E T_1

C	1.613849000	2.022545000	1.173025000
C	1.162216000	-0.846562000	-0.071257000
C	1.449765000	1.735143000	2.433473000
H	2.279630000	1.762017000	3.134781000
H	0.474088000	1.457351000	2.824434000
C	-1.264141000	-0.843616000	0.180714000
H	-1.111370000	-1.677179000	0.860168000
C	-0.174495000	-0.299304000	-0.388071000
H	-0.266610000	0.534605000	-1.065453000
C	1.769125000	2.263464000	-0.098819000
H	1.654930000	3.276510000	-0.479088000
C	-2.651458000	-0.430858000	-0.009544000
C	-3.026672000	0.661944000	-0.812280000
C	-3.660176000	-1.157845000	0.644811000
C	-4.363959000	1.007147000	-0.954963000
H	-2.270263000	1.245596000	-1.322719000
C	-5.000586000	-0.811742000	0.499855000
H	-3.381791000	-2.000326000	1.268721000
C	-5.356688000	0.271809000	-0.300919000
H	-4.637535000	1.852715000	-1.575741000
H	-5.764917000	-1.385499000	1.011256000
H	-6.399309000	0.545426000	-0.415498000
C	2.106856000	1.215334000	-1.132963000
H	3.047096000	1.478405000	-1.612465000
H	1.348351000	1.197890000	-1.917053000
N	2.273671000	-0.137983000	-0.578832000
C	3.607460000	-0.584942000	-0.440745000
O	4.521489000	0.195029000	-0.654927000
C	3.891990000	-2.020956000	-0.094478000
H	3.741187000	-2.188472000	0.972884000
H	3.237847000	-2.711712000	-0.624729000
H	4.935434000	-2.208679000	-0.347404000
O	1.300888000	-1.857795000	0.601513000

1o_E T_1

C	2.546487000	1.493450000	1.767004000
C	2.053377000	-0.755502000	-0.359326000
C	2.207774000	0.841472000	2.843127000
H	2.942358000	0.563927000	3.594365000
H	1.175260000	0.552879000	3.024054000
C	-0.371516000	-0.516978000	-0.244326000
H	-0.368382000	-1.501452000	0.213441000
C	0.808820000	0.013711000	-0.597956000
H	0.863370000	0.993335000	-1.045323000
C	2.871960000	2.106559000	0.663301000
H	2.868824000	3.193875000	0.622976000
C	-1.685351000	0.105418000	-0.398967000
C	-1.876296000	1.381989000	-0.959696000

C	-2.808102000	-0.606191000	0.040396000
C	-3.147952000	1.928256000	-1.079405000
H	-1.024414000	1.954943000	-1.303782000
C	-4.069283000	-0.038268000	-0.089167000
H	-2.697475000	-1.589293000	0.476764000
C	-4.266248000	1.221460000	-0.644116000
H	-3.274645000	2.912388000	-1.513081000
H	-5.261588000	1.633297000	-0.729699000
C	3.273441000	1.411725000	-0.616536000
H	4.287664000	1.705059000	-0.878099000
H	2.632348000	1.731487000	-1.439509000
N	3.266118000	-0.057808000	-0.526996000
C	4.534772000	-0.680631000	-0.454234000
O	5.531252000	0.012567000	-0.335624000
C	4.648534000	-2.174496000	-0.586569000
H	4.384334000	-2.657480000	0.355301000
H	3.984825000	-2.574090000	-1.352124000
H	5.688509000	-2.394640000	-0.827057000
O	2.024355000	-1.930505000	-0.027529000
N	-5.238122000	-0.799410000	0.380095000
O	-6.349065000	-0.297035000	0.240334000
O	-5.046477000	-1.899471000	0.888934000

1y_E T_1

C	2.446764000	2.013335000	1.228292000
C	1.980022000	-0.821067000	-0.039198000
C	2.310626000	1.707103000	2.487666000
H	3.153690000	1.733066000	3.173083000
H	1.346103000	1.412143000	2.893480000
C	-0.442716000	-0.833420000	0.235790000
H	-0.269349000	-1.609919000	0.975770000
C	0.638939000	-0.316280000	-0.379451000
H	0.532996000	0.464862000	-1.116118000
C	2.572031000	2.275708000	-0.042555000
H	2.437151000	3.293597000	-0.402900000
C	-1.832827000	-0.464989000	0.029087000
C	-2.247313000	0.537006000	-0.874108000
C	-2.825545000	-1.132448000	0.761668000
C	-3.583291000	0.844522000	-1.032758000
H	-1.513564000	1.081904000	-1.455692000
C	-4.176634000	-0.834361000	0.612922000
H	-2.531197000	-1.904964000	1.463862000
C	-4.562516000	0.159775000	-0.291673000
H	-3.899944000	1.614516000	-1.726182000
H	-4.909489000	-1.373122000	1.197132000
C	2.902223000	1.251428000	-1.102599000
H	3.836331000	1.528324000	-1.586646000
H	2.133973000	1.251596000	-1.877441000

N	3.079654000	-0.113145000	-0.582026000
C	4.408430000	-0.578452000	-0.505133000
O	5.328374000	0.192553000	-0.731157000
C	4.681501000	-2.030487000	-0.216949000
H	4.622940000	-2.217131000	0.856313000
H	3.966188000	-2.693386000	-0.701474000
H	5.693823000	-2.238758000	-0.563675000
O	2.147892000	-1.797784000	0.678433000
O	-5.844265000	0.532245000	-0.521451000
C	-6.888770000	-0.129974000	0.199991000
H	-6.900018000	-1.201082000	-0.020651000
H	-6.782050000	0.026855000	1.277097000
H	-7.816734000	0.322997000	-0.144325000

1c_TS1 T_1

C	0.488069000	1.771529000	1.081455000
C	1.410464000	-0.680310000	0.203972000
C	-0.524306000	1.624664000	1.940381000
H	-0.358158000	1.227182000	2.937219000
H	-1.547547000	1.823527000	1.641316000
C	-1.087766000	-0.791143000	0.398305000
H	-0.934791000	-1.531424000	1.173613000
C	0.107772000	-0.188130000	-0.170222000
H	0.022981000	0.430596000	-1.052146000
C	1.531223000	2.223064000	0.436198000
H	1.877272000	3.230729000	0.660768000
C	-2.403171000	-0.509566000	-0.009608000
C	-2.725897000	0.453826000	-1.014005000
C	-3.492252000	-1.197855000	0.609450000
C	-4.042033000	0.699851000	-1.364467000
H	-1.935407000	1.005806000	-1.506343000
C	-4.799885000	-0.941148000	0.248806000
H	-3.270988000	-1.932870000	1.375707000
C	-5.090670000	0.010219000	-0.742127000
H	-4.262402000	1.436275000	-2.129402000
H	-5.607480000	-1.477977000	0.733961000
H	-6.117985000	0.209262000	-1.023283000
C	2.298509000	1.482472000	-0.634545000
H	3.283816000	1.923223000	-0.750365000
H	1.784387000	1.582064000	-1.597091000
N	2.505891000	0.060094000	-0.320736000
C	3.794674000	-0.453991000	-0.474714000
O	4.719262000	0.286116000	-0.788551000
C	4.018866000	-1.934606000	-0.305577000
H	4.101161000	-2.181702000	0.754060000
H	3.204503000	-2.530006000	-0.716593000
H	4.956341000	-2.178121000	-0.805069000
O	1.575922000	-1.644926000	0.954675000

1c_TS1 S_0

C	0.148261000	1.621221000	0.789200000
C	1.474789000	-0.694553000	0.196041000
C	-1.034665000	2.014444000	1.292170000
H	-1.257920000	3.073331000	1.374719000
H	-1.798949000	1.316735000	1.603118000
C	-0.977767000	-0.842127000	0.348776000
H	-0.796467000	-1.625369000	1.075788000
C	0.122940000	-0.081362000	-0.073895000
H	0.056946000	0.383006000	-1.055055000
C	1.419728000	2.061376000	0.653590000
H	1.881555000	2.628773000	1.455536000
C	-2.329640000	-0.585391000	-0.019660000
C	-2.693391000	0.468960000	-0.893842000
C	-3.367170000	-1.371861000	0.543205000
C	-4.030321000	0.715932000	-1.186069000
H	-1.927886000	1.078198000	-1.355195000
C	-4.693951000	-1.120929000	0.242591000
H	-3.102559000	-2.176267000	1.220866000
C	-5.033327000	-0.072317000	-0.623224000
H	-4.291410000	1.526247000	-1.857212000
H	-5.473217000	-1.733975000	0.680882000
H	-6.073686000	0.123242000	-0.856267000
C	2.304725000	1.540320000	-0.438479000
H	3.272816000	2.029009000	-0.429079000
H	1.868570000	1.676629000	-1.432010000
N	2.556738000	0.087604000	-0.221758000
C	3.874958000	-0.375694000	-0.383501000
O	4.755722000	0.417768000	-0.675233000
C	4.167795000	-1.844045000	-0.236596000
H	4.116854000	-2.137607000	0.812975000
H	3.448845000	-2.459519000	-0.777411000
H	5.174484000	-2.013407000	-0.616927000
O	1.605161000	-1.781031000	0.730952000

1o_TS1 T_1

C	-1.563359000	-1.583562000	1.432543000
C	-2.241400000	0.721506000	0.005123000
C	-0.462442000	-1.375052000	2.158060000
H	-0.472640000	-0.698663000	3.007556000
H	0.484736000	-1.826602000	1.883148000
C	0.254466000	0.519978000	0.096060000
H	0.247558000	1.419621000	0.698119000
C	-1.039340000	-0.024190000	-0.281989000
H	-1.088325000	-0.846444000	-0.980796000
C	-2.709214000	-2.002407000	0.967469000
H	-3.184984000	-2.844674000	1.467047000

C	1.494845000	-0.014627000	-0.292450000
C	1.640048000	-1.190853000	-1.091277000
C	2.686498000	0.634619000	0.138309000
C	2.892359000	-1.676144000	-1.429412000
H	0.760480000	-1.716899000	-1.438430000
C	3.913206000	0.119918000	-0.218103000
H	2.624993000	1.527886000	0.744394000
C	4.056026000	-1.034420000	-1.002007000
H	2.974565000	-2.569935000	-2.036176000
H	5.036496000	-1.405626000	-1.260725000
C	-3.440239000	-1.438840000	-0.230994000
H	-4.477370000	-1.757579000	-0.208201000
H	-3.001104000	-1.829036000	-1.155459000
N	-3.453125000	0.032461000	-0.263527000
C	-4.686148000	0.663742000	-0.459041000
O	-5.712144000	-0.001053000	-0.519461000
C	-4.722855000	2.157467000	-0.650592000
H	-4.673280000	2.659851000	0.316783000
H	-3.889233000	2.521737000	-1.249863000
H	-5.670402000	2.397739000	-1.132278000
O	-2.225585000	1.855889000	0.486771000
N	5.126009000	0.813483000	0.247112000
O	4.996368000	1.824627000	0.931064000
O	6.214310000	0.343562000	-0.072175000

1o_TS1 S_0

C	1.249887000	1.630743000	0.968856000
C	2.278117000	-0.746483000	0.062686000
C	0.107018000	2.111292000	1.487644000
H	0.023444000	3.168647000	1.717496000
H	-0.755966000	1.488940000	1.677129000
C	-0.177460000	-0.553506000	0.105252000
H	-0.158441000	-1.462286000	0.694674000
C	1.039917000	0.091631000	-0.151477000
H	1.092843000	0.708379000	-1.045572000
C	2.574484000	1.893725000	0.940888000
H	3.065580000	2.270934000	1.832602000
C	-1.450844000	-0.026473000	-0.259818000
C	-1.604061000	1.208135000	-0.939719000
C	-2.619473000	-0.724545000	0.119987000
C	-2.868270000	1.717258000	-1.223579000
H	-0.731589000	1.757218000	-1.265259000
C	-3.857696000	-0.193030000	-0.181511000
H	-2.541927000	-1.664993000	0.647855000
C	-4.013638000	1.026948000	-0.848282000
H	-2.962518000	2.661621000	-1.745428000
H	-5.000615000	1.409152000	-1.065055000
C	3.437628000	1.414483000	-0.187960000

H	4.460344000	1.756452000	-0.074289000
H	3.074547000	1.752316000	-1.162077000
N	3.479253000	-0.073623000	-0.179024000
C	4.736323000	-0.690023000	-0.337382000
O	5.730111000	0.007019000	-0.459496000
C	4.823109000	-2.190238000	-0.393467000
H	4.640447000	-2.618443000	0.593219000
H	4.081339000	-2.615074000	-1.070024000
H	5.829051000	-2.444748000	-0.724990000
O	2.220889000	-1.911673000	0.410596000
N	-5.061527000	-0.937744000	0.222904000
O	-4.916395000	-2.028209000	0.766890000
O	-6.155963000	-0.430643000	-0.004260000

1y_TS1 T_1

C	1.295455000	1.679820000	1.165352000
C	2.204606000	-0.692936000	0.180081000
C	0.386567000	1.515348000	2.131469000
H	0.689425000	1.264419000	3.143946000
H	-0.675493000	1.533911000	1.914938000
C	-0.284293000	-0.869775000	0.420856000
H	-0.102541000	-1.687047000	1.107481000
C	0.881381000	-0.206298000	-0.130025000
H	0.763042000	0.439870000	-0.988578000
C	2.262466000	2.202006000	0.451133000
H	2.515280000	3.249318000	0.609921000
C	-1.610067000	-0.537845000	0.107364000
C	-1.972707000	0.546681000	-0.755726000
C	-2.686495000	-1.284716000	0.677511000
C	-3.290124000	0.843613000	-1.016870000
H	-1.201256000	1.154915000	-1.210110000
C	-4.008409000	-0.987337000	0.414923000
H	-2.448957000	-2.111674000	1.337643000
C	-4.326997000	0.084856000	-0.439538000
H	-3.554324000	1.667281000	-1.670059000
H	-4.788689000	-1.582498000	0.869447000
C	3.040374000	1.502519000	-0.634791000
H	4.018398000	1.963780000	-0.738100000
H	2.527464000	1.624831000	-1.596736000
N	3.272294000	0.075941000	-0.363939000
C	4.555807000	-0.420129000	-0.591422000
O	5.457533000	0.337556000	-0.931755000
C	4.804500000	-1.901540000	-0.467910000
H	4.929108000	-2.175003000	0.580979000
H	3.982207000	-2.496729000	-0.863373000
H	5.725132000	-2.120240000	-1.008582000
O	2.411300000	-1.678648000	0.892253000
O	-5.588028000	0.459709000	-0.762846000

C	-6.685992000	-0.281467000	-0.219241000
H	-6.652307000	-1.325332000	-0.543184000
H	-6.691824000	-0.230345000	0.873095000
H	-7.583604000	0.193224000	-0.611366000

1o_TS1 S_0

C	0.981234000	1.623134000	0.844819000
C	2.246554000	-0.701094000	0.201522000
C	-0.174862000	2.030395000	1.401211000
H	-0.382768000	3.091703000	1.490883000
H	-0.929977000	1.341461000	1.751618000
C	-0.201006000	-0.812394000	0.437868000
H	-0.007584000	-1.605213000	1.151510000
C	0.898859000	-0.064166000	-0.015103000
H	0.805955000	0.401480000	-0.993568000
C	2.248877000	2.056423000	0.653224000
H	2.746269000	2.626843000	1.431092000
C	-1.553422000	-0.531921000	0.117950000
C	-1.936989000	0.530617000	-0.744872000
C	-2.589863000	-1.297368000	0.707423000
C	-3.268110000	0.796075000	-0.999899000
H	-1.181103000	1.132364000	-1.230918000
C	-3.923472000	-1.038642000	0.454798000
H	-2.323009000	-2.107289000	1.377485000
C	-4.273074000	0.018257000	-0.405794000
H	-3.558041000	1.603650000	-1.661438000
H	-4.684470000	-1.647259000	0.923010000
C	3.085823000	1.521097000	-0.469080000
H	4.062261000	1.992628000	-0.492922000
H	2.620794000	1.664393000	-1.448677000
N	3.322552000	0.061786000	-0.265941000
C	4.621852000	-0.424650000	-0.487396000
O	5.503171000	0.351519000	-0.823084000
C	4.895953000	-1.897987000	-0.349445000
H	4.895725000	-2.186175000	0.702898000
H	4.138561000	-2.502959000	-0.847923000
H	5.878035000	-2.087044000	-0.781454000
O	2.382921000	-1.785726000	0.740412000
O	-5.544609000	0.352760000	-0.719164000
C	-6.618812000	-0.422603000	-0.172770000
H	-6.549468000	-1.466009000	-0.492002000
H	-6.627842000	-0.365427000	0.919010000
H	-7.530312000	0.020897000	-0.569058000

1c_intermediate T_1

C	0.327200000	1.547625000	0.744769000
C	1.400326000	-0.649952000	0.174994000
C	-0.570804000	2.083656000	1.642993000

H	-0.386041000	3.060405000	2.075698000
H	-1.468640000	1.557464000	1.937087000
C	-1.064746000	-0.600477000	0.578650000
H	-0.884861000	-1.325407000	1.362515000
C	0.108853000	0.175194000	0.083970000
H	-0.012462000	0.380180000	-0.989669000
C	1.495362000	2.179101000	0.339965000
H	1.749641000	3.175315000	0.681133000
C	-2.384404000	-0.441925000	0.107783000
C	-2.747990000	0.501913000	-0.895217000
C	-3.426465000	-1.247319000	0.653663000
C	-4.061587000	0.619300000	-1.319694000
H	-1.991957000	1.145796000	-1.327428000
C	-4.734469000	-1.119924000	0.220829000
H	-3.174607000	-1.971637000	1.420870000
C	-5.065844000	-0.186802000	-0.770431000
H	-4.313129000	1.346486000	-2.083966000
H	-5.506958000	-1.747145000	0.652032000
H	-6.090914000	-0.088299000	-1.107945000
C	2.413957000	1.473476000	-0.597314000
H	3.411173000	1.900824000	-0.576333000
H	2.055981000	1.540801000	-1.635051000
N	2.544446000	0.037906000	-0.236173000
C	3.824319000	-0.536774000	-0.396801000
O	4.722323000	0.146358000	-0.860837000
C	4.059027000	-1.965954000	0.002932000
H	3.818145000	-2.126184000	1.054250000
H	3.426934000	-2.642284000	-0.574214000
H	5.109728000	-2.185113000	-0.183026000
O	1.403982000	-1.805529000	0.550925000

1c_intermediate S_0

C	0.264488000	1.487503000	0.725526000
C	1.426997000	-0.665280000	0.129958000
C	-0.695363000	1.988074000	1.581929000
H	-0.552924000	2.960384000	2.040103000
H	-1.598180000	1.443169000	1.817585000
C	-1.044767000	-0.702109000	0.476759000
H	-0.840422000	-1.513177000	1.163645000
C	0.113145000	0.123878000	0.029000000
H	0.009874000	0.349822000	-1.043820000
C	1.437228000	2.153765000	0.404527000
H	1.663774000	3.129619000	0.816823000
C	-2.376189000	-0.490693000	0.064306000
C	-2.756663000	0.551062000	-0.829430000
C	-3.411402000	-1.334712000	0.562549000
C	-4.082246000	0.726357000	-1.194869000
H	-2.003721000	1.219608000	-1.227926000

C	-4.730446000	-1.148628000	0.189852000
H	-3.145450000	-2.134346000	1.245561000
C	-5.079551000	-0.116789000	-0.692230000
H	-4.347439000	1.527499000	-1.876040000
H	-5.498321000	-1.805776000	0.583014000
H	-6.113739000	0.027283000	-0.982319000
C	2.412267000	1.512312000	-0.521778000
H	3.396136000	1.962267000	-0.438654000
H	2.098086000	1.615804000	-1.570209000
N	2.564482000	0.066101000	-0.216096000
C	3.861930000	-0.471813000	-0.363498000
O	4.753557000	0.249265000	-0.779716000
C	4.123423000	-1.907952000	-0.007456000
H	3.856356000	-2.112089000	1.029840000
H	3.527380000	-2.579758000	-0.626530000
H	5.184694000	-2.092815000	-0.169077000
O	1.450871000	-1.835521000	0.457191000

1o_intermediate T_1

C	1.433089000	1.522566000	0.953167000
C	2.213342000	-0.686292000	0.041860000
C	0.568923000	2.026425000	1.901714000
H	0.865622000	2.875541000	2.506777000
H	-0.410353000	1.599623000	2.070614000
C	-0.235062000	-0.327514000	0.364791000
H	-0.213347000	-1.192275000	1.015464000
C	1.063760000	0.331536000	0.051887000
H	1.038246000	0.730769000	-0.972455000
C	2.702371000	2.027584000	0.706166000
H	3.077051000	2.899697000	1.228033000
C	-1.486226000	0.115568000	-0.111097000
C	-1.650028000	1.255529000	-0.949542000
C	-2.658635000	-0.593485000	0.263804000
C	-2.903452000	1.652395000	-1.387202000
H	-0.781498000	1.828462000	-1.247989000
C	-3.890941000	-0.167551000	-0.191217000
H	-2.583673000	-1.463042000	0.901778000
C	-4.050402000	0.948748000	-1.017505000
H	-2.998910000	2.523501000	-2.024104000
H	-5.032134000	1.250053000	-1.351982000
C	3.563417000	1.357373000	-0.308381000
H	4.608461000	1.620399000	-0.181587000
H	3.278880000	1.649320000	-1.329853000
N	3.466094000	-0.121561000	-0.197403000
C	4.659960000	-0.849398000	-0.403355000
O	5.674183000	-0.242485000	-0.703208000
C	4.659827000	-2.343941000	-0.250957000
H	4.327833000	-2.638916000	0.744948000

H	3.978022000	-2.809895000	-0.963693000
H	5.678362000	-2.687218000	-0.427652000
O	2.021816000	-1.875130000	0.204876000
N	-5.088872000	-0.924548000	0.212540000
O	-6.179845000	-0.538632000	-0.196693000
O	-4.942751000	-1.903819000	0.937641000

1o_intermediate S_0

C	1.385454000	1.507192000	0.886514000
C	2.232979000	-0.696634000	0.002896000
C	0.477702000	2.020437000	1.790388000
H	0.745954000	2.882428000	2.390648000
H	-0.504419000	1.592081000	1.930922000
C	-0.226218000	-0.388325000	0.276650000
H	-0.186347000	-1.320326000	0.824793000
C	1.063441000	0.299605000	-0.010652000
H	1.048324000	0.692090000	-1.039377000
C	2.658043000	2.021325000	0.688747000
H	3.013346000	2.880346000	1.244821000
C	-1.487138000	0.098165000	-0.124883000
C	-1.665904000	1.315763000	-0.842353000
C	-2.652335000	-0.643130000	0.206884000
C	-2.929111000	1.756464000	-1.206414000
H	-0.802830000	1.912620000	-1.107111000
C	-3.893362000	-0.172781000	-0.173195000
H	-2.564483000	-1.571975000	0.753091000
C	-4.068389000	1.021151000	-0.880198000
H	-3.037196000	2.686643000	-1.751072000
H	-5.057153000	1.354614000	-1.158858000
C	3.559899000	1.368837000	-0.302141000
H	4.596109000	1.648622000	-0.143753000
H	3.301063000	1.656462000	-1.331039000
N	3.482835000	-0.111339000	-0.193326000
C	4.695480000	-0.819477000	-0.355168000
O	5.705675000	-0.197657000	-0.637269000
C	4.720896000	-2.310362000	-0.172401000
H	4.344298000	-2.594932000	0.810523000
H	4.087572000	-2.804698000	-0.910342000
H	5.754474000	-2.633143000	-0.290950000
O	2.056306000	-1.890788000	0.143415000
N	-5.083851000	-0.965007000	0.180882000
O	-6.181019000	-0.548933000	-0.179416000
O	-4.925990000	-2.002097000	0.817867000

1y_intermediate T_1

C	1.177758000	1.535525000	0.793599000
C	2.179064000	-0.673892000	0.153938000
C	0.345472000	2.074330000	1.751295000

H	0.571487000	3.043194000	2.182302000
H	-0.540163000	1.556947000	2.093975000
C	-0.266860000	-0.586377000	0.671683000
H	-0.064136000	-1.345841000	1.416054000
C	0.898803000	0.172763000	0.134022000
H	0.734848000	0.391500000	-0.931874000
C	2.328847000	2.154057000	0.324044000
H	2.622032000	3.141872000	0.658388000
C	-1.603112000	-0.369278000	0.284445000
C	-1.997204000	0.623874000	-0.662043000
C	-2.646407000	-1.153485000	0.851609000
C	-3.319426000	0.802158000	-1.008769000
H	-1.249232000	1.261395000	-1.116813000
C	-3.975793000	-0.976342000	0.504910000
H	-2.386584000	-1.917025000	1.576916000
C	-4.326005000	0.006688000	-0.433088000
H	-3.606178000	1.561097000	-1.727727000
H	-4.731431000	-1.600615000	0.962263000
C	3.175746000	1.436103000	-0.669886000
H	4.177006000	1.851070000	-0.718471000
H	2.748603000	1.501542000	-1.681158000
N	3.312005000	0.000564000	-0.310058000
C	4.580974000	-0.583191000	-0.512153000
O	5.467317000	0.089478000	-1.013029000
C	4.821014000	-2.010855000	-0.108994000
H	4.610574000	-2.162766000	0.950072000
H	4.169064000	-2.688305000	-0.662144000
H	5.864746000	-2.236414000	-0.324221000
O	2.185231000	-1.832035000	0.521750000
O	-5.596766000	0.263889000	-0.842741000
C	-6.659739000	-0.520450000	-0.295603000
H	-6.533053000	-1.579830000	-0.537835000
H	-6.725446000	-0.394182000	0.789150000
H	-7.571219000	-0.148016000	-0.760366000

1y_intermediate S_0

C	1.118909000	1.498045000	0.773940000
C	2.199116000	-0.680211000	0.125451000
C	0.218011000	2.018102000	1.681193000
H	0.402195000	2.988551000	2.128407000
H	-0.680001000	1.488627000	1.965705000
C	-0.255611000	-0.662669000	0.591793000
H	-0.039058000	-1.483646000	1.262776000
C	0.899422000	0.136763000	0.090668000
H	0.751193000	0.366514000	-0.976252000
C	2.284796000	2.139440000	0.383999000
H	2.558297000	3.109723000	0.780725000
C	-1.596169000	-0.416159000	0.240141000

C	-1.997025000	0.642376000	-0.629519000
C	-2.635655000	-1.232755000	0.767273000
C	-3.323744000	0.852596000	-0.941621000
H	-1.250888000	1.301026000	-1.055980000
C	-3.968351000	-1.023705000	0.455335000
H	-2.369718000	-2.046498000	1.433350000
C	-4.326062000	0.025564000	-0.406169000
H	-3.615963000	1.659926000	-1.603386000
H	-4.721312000	-1.674054000	0.879518000
C	3.187552000	1.472259000	-0.596643000
H	4.182660000	1.904251000	-0.582331000
H	2.807699000	1.569597000	-1.623594000
N	3.332277000	0.026610000	-0.284079000
C	4.613614000	-0.532994000	-0.477780000
O	5.499790000	0.168404000	-0.937817000
C	4.867323000	-1.969246000	-0.115608000
H	4.635405000	-2.159073000	0.932758000
H	4.239275000	-2.638204000	-0.705493000
H	5.919162000	-2.171489000	-0.313973000
O	2.217657000	-1.849268000	0.457271000
O	-5.601001000	0.317394000	-0.776578000
C	-6.660612000	-0.501591000	-0.275233000
H	-6.541406000	-1.540319000	-0.597246000
H	-6.712050000	-0.455969000	0.816587000
H	-7.576081000	-0.092361000	-0.699357000

1c_TS2 T_1

C	-0.577562000	1.760470000	0.531091000
C	-1.283144000	-0.386708000	-0.574784000
C	0.714600000	2.375369000	0.569841000
H	0.898812000	3.345954000	0.114800000
H	1.380210000	2.110646000	1.384034000
C	1.073475000	0.695803000	-0.398195000
H	0.915097000	1.060482000	-1.410042000
C	-0.210501000	0.315627000	0.295012000
H	-0.056449000	-0.266998000	1.208959000
C	-1.792260000	2.260684000	0.175374000
H	-1.967758000	3.331281000	0.144874000
C	2.376439000	0.124174000	-0.150358000
C	2.665656000	-0.646604000	0.997000000
C	3.408111000	0.344818000	-1.092375000
C	3.924610000	-1.201972000	1.171259000
H	1.902481000	-0.807550000	1.748250000
C	4.665707000	-0.207599000	-0.908720000
H	3.196979000	0.941710000	-1.972756000
C	4.930443000	-0.985283000	0.223551000
H	4.131224000	-1.801219000	2.050468000
H	5.443116000	-0.039422000	-1.644978000

H	5.914909000	-1.414292000	0.369647000
C	-2.946802000	1.381145000	-0.137541000
H	-3.365973000	1.669940000	-1.111425000
H	-3.748886000	1.556873000	0.587809000
N	-2.606848000	-0.040417000	-0.113879000
C	-3.644303000	-0.926775000	0.078558000
O	-4.817017000	-0.530937000	0.110862000
C	-3.310451000	-2.385296000	0.272168000
H	-3.197133000	-2.881419000	-0.694462000
H	-2.381633000	-2.530177000	0.822752000
H	-4.141312000	-2.844348000	0.809144000
O	-1.012964000	-1.501020000	-1.101013000

1c_TS2 S_1

C	0.661330000	2.084131000	-0.214904000
C	1.177853000	-0.424596000	-0.559380000
C	-0.472050000	2.911023000	0.011512000
H	-0.397335000	3.828903000	0.587091000
H	-1.358206000	2.782359000	-0.596064000
C	-0.898921000	0.548688000	0.471061000
H	-0.536566000	0.594317000	1.492243000
C	0.171794000	0.715904000	-0.586952000
H	-0.269418000	0.712747000	-1.586397000
C	1.944465000	2.291034000	0.141454000
H	2.263814000	3.237809000	0.564013000
C	-2.216917000	0.037650000	0.261389000
C	-2.748607000	-0.227040000	-1.022885000
C	-3.053223000	-0.191571000	1.382965000
C	-4.048093000	-0.693054000	-1.171052000
H	-2.137540000	-0.073604000	-1.903123000
C	-4.348745000	-0.657282000	1.226238000
H	-2.661577000	0.004759000	2.375259000
C	-4.856773000	-0.910315000	-0.052707000
H	-4.434575000	-0.892820000	-2.164222000
H	-4.969086000	-0.828216000	2.098938000
H	-5.869660000	-1.276121000	-0.174724000
C	2.991805000	1.239566000	0.001027000
H	3.668315000	1.272796000	0.854512000
H	3.615189000	1.408243000	-0.885875000
N	2.455417000	-0.145290000	-0.071144000
C	3.405882000	-1.152652000	0.212769000
O	4.576071000	-0.834669000	0.340084000
C	2.956050000	-2.572452000	0.423513000
H	2.007787000	-2.634351000	0.955782000
H	2.822854000	-3.069945000	-0.538591000
H	3.743482000	-3.077829000	0.982830000
O	0.840115000	-1.536108000	-0.928579000

1o_TS2 T_1

C	-1.480257000	1.863382000	0.485874000
C	-2.137954000	-0.560423000	0.016295000
C	-0.164389000	2.459942000	0.520620000
H	0.111303000	3.273430000	-0.143594000
H	0.411122000	2.376208000	1.435393000
C	0.178252000	0.557396000	-0.067465000
H	0.083119000	0.694192000	-1.140174000
C	-1.156202000	0.407901000	0.651492000
H	-1.038728000	0.102941000	1.694560000
C	-2.639148000	2.283596000	-0.041182000
H	-2.795558000	3.318178000	-0.325620000
C	1.454455000	0.122849000	0.396544000
C	1.674963000	-0.328899000	1.741107000
C	2.527927000	0.175132000	-0.514660000
C	2.942462000	-0.748730000	2.107479000
H	0.862301000	-0.347938000	2.453376000
C	3.799913000	-0.243748000	-0.130113000
H	2.365931000	0.528080000	-1.523525000
C	4.006628000	-0.716643000	1.205823000
H	3.120054000	-1.106607000	3.114915000
C	-3.779932000	1.354964000	-0.242695000
H	-4.214605000	1.534775000	-1.229291000
H	-4.576819000	1.565509000	0.477981000
N	-3.438421000	-0.089528000	-0.156484000
C	-4.544275000	-0.947390000	-0.397610000
O	-5.597681000	-0.442299000	-0.737447000
C	-4.411748000	-2.426293000	-0.170282000
H	-3.934938000	-2.895952000	-1.032784000
H	-3.809045000	-2.662179000	0.705706000
H	-5.419866000	-2.824349000	-0.057635000
O	-1.783562000	-1.686845000	-0.266303000
H	4.995936000	-1.039523000	1.494682000
N	4.856880000	-0.202947000	-1.034499000
O	4.655348000	0.226926000	-2.223997000
O	6.011695000	-0.596238000	-0.641562000

1o_TS2 S_1

C	-1.682172000	2.112592000	-0.065625000
C	-2.091867000	-0.348276000	0.613846000
C	-0.581025000	2.993726000	-0.240101000
H	-0.601144000	3.786180000	-0.982270000
H	0.182433000	3.055058000	0.524428000
C	0.075872000	0.647415000	-0.187564000
H	-0.083510000	0.486980000	-1.247934000
C	-1.185184000	0.874203000	0.618885000
H	-0.947294000	1.072706000	1.666426000
C	-2.889863000	2.141493000	-0.661580000

H	-3.185681000	2.973823000	-1.291242000
C	1.364635000	0.321286000	0.337978000
C	1.667127000	0.309505000	1.721073000
C	2.408695000	0.021826000	-0.566320000
C	2.947723000	0.020416000	2.174768000
H	0.890794000	0.520281000	2.444615000
C	3.672750000	-0.261080000	-0.082303000
H	2.219860000	0.017339000	-1.630832000
C	3.975411000	-0.268058000	1.280535000
H	3.151534000	0.014288000	3.238590000
H	4.975155000	-0.496275000	1.619973000
C	-3.881488000	1.040328000	-0.507912000
H	-4.390562000	0.866440000	-1.455672000
H	-4.665243000	1.307416000	0.211284000
N	-3.293382000	-0.259304000	-0.087846000
C	-4.141819000	-1.372036000	-0.308189000
O	-5.288622000	-1.166861000	-0.665766000
C	-3.606314000	-2.769526000	-0.165165000
H	-2.597163000	-2.868772000	-0.563299000
H	-3.568225000	-3.052276000	0.888070000
H	-4.293630000	-3.431046000	-0.692435000
O	-1.735068000	-1.358773000	1.194678000
N	4.742904000	-0.568726000	-1.046411000
O	5.871522000	-0.773090000	-0.609565000
O	4.458560000	-0.606129000	-2.239830000

1y_TS2 T_1

C	-1.432723000	1.906093000	0.273654000
C	-2.003207000	-0.527100000	-0.151978000
C	-0.133167000	2.522776000	-0.059084000
H	-0.076121000	3.279257000	-0.839077000
H	0.540698000	2.702784000	0.775458000
C	0.245354000	0.710275000	-0.516748000
H	0.006216000	0.756903000	-1.578574000
C	-0.993467000	0.471884000	0.357822000
H	-0.728258000	0.177837000	1.378843000
C	-2.710832000	2.251630000	0.179819000
H	-3.033992000	3.267993000	-0.018186000
C	1.549907000	0.264859000	-0.222000000
C	1.961705000	-0.259689000	1.059151000
C	2.632843000	0.538417000	-1.219821000
C	3.249044000	-0.598664000	1.304519000
H	1.219156000	-0.411291000	1.833629000
C	3.932629000	0.173766000	-0.964303000
H	2.360938000	0.999883000	-2.160811000
C	4.271975000	-0.415166000	0.266916000
H	3.559206000	-1.017829000	2.253951000
H	4.696422000	0.352634000	-1.710874000

C	-3.783225000	1.219585000	0.346519000
H	-4.615033000	1.438579000	-0.322412000
H	-4.194969000	1.235335000	1.361655000
N	-3.347912000	-0.175138000	0.042009000
C	-4.412804000	-1.098016000	-0.034959000
O	-5.553660000	-0.684726000	0.099301000
C	-4.138684000	-2.563784000	-0.232639000
H	-3.794037000	-2.756377000	-1.249389000
H	-3.364555000	-2.928939000	0.442402000
H	-5.075375000	-3.091187000	-0.055063000
O	-1.657265000	-1.569473000	-0.677095000
O	5.510087000	-0.807230000	0.643816000
C	6.587427000	-0.661666000	-0.288543000
H	6.393070000	-1.237280000	-1.197702000
H	6.742164000	0.391185000	-0.539844000
H	7.469900000	-1.053275000	0.213810000

1y_TS2 S_1

C	-1.669927000	2.121649000	0.177922000
C	-1.874819000	-0.425335000	0.574759000
C	-0.642889000	3.082866000	-0.024256000
H	-0.815771000	3.980811000	-0.610373000
H	0.228941000	3.075037000	0.616950000
C	0.086499000	0.777856000	-0.435148000
H	-0.253989000	0.784397000	-1.464724000
C	-1.022838000	0.834147000	0.593666000
H	-0.609773000	0.910892000	1.602536000
C	-2.955143000	2.150934000	-0.227441000
H	-3.379996000	3.040531000	-0.680617000
C	1.436472000	0.391567000	-0.191240000
C	1.964744000	0.172854000	1.106719000
C	2.324926000	0.240831000	-1.281933000
C	3.288445000	-0.171443000	1.292398000
H	1.324322000	0.265134000	1.974311000
C	3.655463000	-0.103479000	-1.104437000
H	1.950795000	0.401328000	-2.287257000
C	4.149287000	-0.312991000	0.191670000
H	3.683291000	-0.342827000	2.286956000
H	4.297780000	-0.209164000	-1.967722000
C	-3.862881000	0.974361000	-0.105408000
H	-4.494672000	0.899171000	-0.990258000
H	-4.547068000	1.078757000	0.745902000
N	-3.158307000	-0.327524000	0.033386000
C	-3.962140000	-1.455688000	-0.245224000
O	-5.157272000	-1.294048000	-0.426997000
C	-3.330294000	-2.813847000	-0.383781000
H	-2.363514000	-2.773993000	-0.883879000
H	-3.169327000	-3.254529000	0.601450000

H	-4.027334000	-3.435306000	-0.946081000
O	-1.413851000	-1.473113000	0.994832000
O	5.429503000	-0.656048000	0.477173000
C	6.351434000	-0.820887000	-0.605333000
H	6.029300000	-1.621143000	-1.277701000
H	6.470125000	0.110886000	-1.165778000
H	7.299957000	-1.092004000	-0.145066000

2c_final product S_0

C	0.509395000	1.912001000	-0.131877000
C	1.238290000	-0.502981000	0.051563000
C	-0.850080000	2.243372000	0.436109000
H	-0.885175000	2.863575000	1.332258000
H	-1.523602000	2.658743000	-0.318947000
C	-1.071375000	0.696738000	0.608904000
H	-0.794163000	0.398641000	1.623821000
C	0.155238000	0.467978000	-0.339682000
H	-0.163289000	0.239214000	-1.363661000
C	1.756473000	2.349414000	-0.178517000
H	2.067259000	3.350094000	0.100336000
C	-2.394452000	0.086332000	0.238349000
C	-2.456774000	-1.234270000	-0.222368000
C	-3.585083000	0.807204000	0.372725000
C	-3.680252000	-1.818459000	-0.543728000
H	-1.540048000	-1.804951000	-0.321924000
C	-4.811335000	0.223577000	0.053331000
H	-3.556820000	1.830952000	0.729069000
C	-4.863149000	-1.090906000	-0.407674000
H	-3.710333000	-2.841990000	-0.900997000
H	-5.724880000	0.797724000	0.162387000
H	-5.815202000	-1.544256000	-0.659703000
C	2.810452000	1.367277000	-0.614551000
H	3.780897000	1.646289000	-0.214260000
H	2.913938000	1.345612000	-1.705241000
N	2.545124000	-0.027570000	-0.137982000
C	3.702560000	-0.827977000	-0.000809000
O	4.782896000	-0.356518000	-0.316885000
C	3.598312000	-2.231440000	0.527837000
H	3.131586000	-2.251189000	1.512786000
H	2.984531000	-2.852438000	-0.125922000
H	4.610721000	-2.630432000	0.579451000
O	0.974530000	-1.605953000	0.496729000

2o_final product S_0

C	1.290855000	1.857021000	-0.145264000
C	2.212390000	-0.497443000	0.012556000
C	-0.086868000	2.071961000	0.435785000
H	-0.167420000	2.680924000	1.336372000

H	-0.797373000	2.435713000	-0.312006000
C	-0.175121000	0.513557000	0.603081000
H	0.135491000	0.231414000	1.612327000
C	1.054373000	0.390782000	-0.362502000
H	0.742330000	0.144620000	-1.384341000
C	2.498701000	2.392650000	-0.195599000
H	2.731440000	3.412589000	0.088881000
C	-1.439388000	-0.213622000	0.243233000
C	-1.390232000	-1.566942000	-0.119282000
C	-2.676000000	0.425519000	0.284073000
C	-2.549913000	-2.269115000	-0.438454000
H	-0.429437000	-2.068733000	-0.145016000
C	-3.823954000	-0.295423000	-0.036620000
H	-2.759644000	1.466701000	0.560639000
C	-3.788564000	-1.637184000	-0.400615000
H	-2.490599000	-3.313759000	-0.718720000
H	-4.699824000	-2.163066000	-0.647009000
C	3.622746000	1.496170000	-0.642658000
H	4.573146000	1.853287000	-0.257392000
H	3.711775000	1.475375000	-1.734508000
N	3.474282000	0.087848000	-0.154269000
C	4.695060000	-0.608771000	0.011519000
O	5.733724000	-0.056231000	-0.310300000
C	4.703336000	-1.998272000	0.584595000
H	4.195160000	-2.036057000	1.548176000
H	4.184188000	-2.694808000	-0.075286000
H	5.746199000	-2.294464000	0.692105000
O	2.033575000	-1.629596000	0.427270000
N	-5.121914000	0.392341000	0.011756000
O	-6.134024000	-0.259096000	-0.232321000
O	-5.136593000	1.587873000	0.294137000

2y_final product S_0

C	1.425036000	1.950815000	-0.158305000
C	1.962757000	-0.502752000	0.105123000
C	0.117781000	2.416080000	0.437450000
H	0.163852000	3.073592000	1.306203000
H	-0.543996000	2.855514000	-0.314436000
C	-0.224190000	0.902011000	0.683985000
H	0.067102000	0.623402000	1.700564000
C	0.946255000	0.534158000	-0.292555000
H	0.575105000	0.290961000	-1.295356000
C	2.700946000	2.281806000	-0.263644000
H	3.100803000	3.264103000	-0.037732000
C	-1.603574000	0.388790000	0.377542000
C	-1.797272000	-0.957529000	0.033359000
C	-2.725920000	1.211321000	0.452120000
C	-3.064113000	-1.457144000	-0.229785000

H	-0.940267000	-1.619810000	-0.023230000
C	-4.010825000	0.724745000	0.192947000
H	-2.612579000	2.256694000	0.717169000
C	-4.182512000	-0.616828000	-0.152196000
H	-3.207961000	-2.497539000	-0.498068000
H	-4.855518000	1.396681000	0.260077000
C	3.658785000	1.203852000	-0.693403000
H	4.658032000	1.412920000	-0.321556000
H	3.735579000	1.146204000	-1.785063000
N	3.293445000	-0.152711000	-0.174703000
C	4.379361000	-1.053174000	-0.087707000
O	5.482835000	-0.678348000	-0.450541000
C	4.172303000	-2.447513000	0.435289000
H	3.799544000	-2.432788000	1.459787000
H	3.437374000	-2.989125000	-0.161369000
H	5.136670000	-2.952373000	0.391916000
O	1.634315000	-1.552478000	0.628750000
O	-5.386844000	-1.193967000	-0.431326000
C	-6.556537000	-0.378151000	-0.358954000
H	-6.700732000	0.018708000	0.650762000
H	-6.508956000	0.447918000	-1.075393000
H	-7.390299000	-1.030670000	-0.614004000

1d-i S_0

C	1.295329000	2.048691000	1.092607000
C	0.794101000	-0.884128000	0.015599000
C	1.125343000	1.828712000	2.365469000
H	1.954228000	1.881621000	3.066430000
H	0.146128000	1.581436000	2.767751000
C	-1.632914000	-0.820482000	0.261276000
H	-1.489923000	-1.567611000	1.036709000
C	-0.536145000	-0.361501000	-0.364766000
H	-0.614020000	0.386337000	-1.138714000
C	1.457518000	2.221243000	-0.189251000
H	1.355033000	3.213360000	-0.624205000
C	-3.016106000	-0.419801000	0.019243000
C	-3.380790000	0.564456000	-0.917521000
C	-4.031835000	-1.045954000	0.761052000
C	-4.714583000	0.902929000	-1.103492000
H	-2.619285000	1.068723000	-1.500052000
C	-5.368716000	-0.706722000	0.572899000
H	-3.761764000	-1.804740000	1.487486000
C	-5.714371000	0.268684000	-0.360463000
H	-4.979909000	1.664070000	-1.828369000
H	-6.138405000	-1.202197000	1.153449000
H	-6.754190000	0.536270000	-0.509629000
C	1.776712000	1.113023000	-1.165079000
H	2.711535000	1.335237000	-1.674748000

H	1.012780000	1.071174000	-1.943696000
N	1.906891000	-0.218676000	-0.548661000
C	3.192320000	-0.756470000	-0.362344000
O	0.933432000	-1.822546000	0.781682000
O	3.456279000	-1.932182000	-0.301070000
O	4.108515000	0.223741000	-0.289307000
C	5.484134000	-0.204892000	-0.199958000
H	5.644598000	-0.773038000	0.716654000
H	5.751180000	-0.811515000	-1.066012000
H	6.068007000	0.712780000	-0.184488000

1d-ii S_0

C	1.194915000	2.368494000	0.982727000
C	0.913563000	-0.607908000	0.091248000
C	1.072885000	2.208606000	2.270053000
H	1.908529000	2.374874000	2.944694000
H	0.129176000	1.897713000	2.711224000
C	-1.510197000	-0.696048000	0.368809000
H	-1.303715000	-1.252172000	1.279026000
C	-0.456481000	-0.279549000	-0.353632000
H	-0.594011000	0.291062000	-1.260280000
C	1.308043000	2.486179000	-0.310502000
H	1.104428000	3.441791000	-0.789689000
C	-2.922460000	-0.475661000	0.070947000
C	-3.370706000	0.207335000	-1.074445000
C	-3.879992000	-0.969084000	0.972865000
C	-4.728378000	0.388705000	-1.302180000
H	-2.656220000	0.596409000	-1.789773000
C	-5.240793000	-0.786632000	0.743610000
H	-3.545547000	-1.498833000	1.858275000
C	-5.669283000	-0.106428000	-0.394654000
H	-5.058565000	0.917115000	-2.189289000
H	-5.964302000	-1.174543000	1.451424000
H	-6.727976000	0.038130000	-0.577265000
C	1.710352000	1.368820000	-1.244043000
H	2.630198000	1.643297000	-1.757754000
H	0.951022000	1.240372000	-2.017100000
N	1.954401000	0.078278000	-0.580629000
C	3.305235000	-0.269023000	-0.416020000
O	4.207611000	0.540655000	-0.468563000
O	1.141878000	-1.407190000	0.983172000
O	3.479279000	-1.580326000	-0.280554000
C	4.832837000	-2.016154000	-0.031843000
H	5.472969000	-1.776661000	-0.881632000
H	5.222188000	-1.547828000	0.872680000
H	4.763633000	-3.093683000	0.099787000

1d-iii S_0

C	-2.861024000	-1.467209000	1.680161000
C	-0.740490000	-0.925105000	-0.849508000
C	-2.151504000	-1.227678000	2.747670000
H	-2.377941000	-0.389378000	3.401728000
H	-1.312765000	-1.861684000	3.023560000
C	1.682067000	-0.754471000	-0.648470000
H	1.723144000	-1.651172000	-1.260194000
C	0.471403000	-0.241739000	-0.369033000
H	0.355730000	0.654737000	0.217957000
C	-3.540304000	-1.682276000	0.589149000
H	-4.417260000	-2.325994000	0.609332000
C	2.973278000	-0.229209000	-0.212840000
C	3.108311000	0.952750000	0.538156000
C	4.135663000	-0.938417000	-0.558814000
C	4.362915000	1.400554000	0.930243000
H	2.230310000	1.525279000	0.811378000
C	5.392618000	-0.489252000	-0.163923000
H	4.043134000	-1.849319000	-1.140380000
C	5.510205000	0.681765000	0.582455000
H	4.450958000	2.314166000	1.507128000
H	6.277838000	-1.051137000	-0.439098000
H	6.487232000	1.036031000	0.890719000
C	-3.188530000	-1.100803000	-0.762339000
H	-4.019818000	-0.513349000	-1.146107000
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N	-1.984827000	-0.257046000	-0.728910000
C	-2.099570000	1.119660000	-0.558193000
O	-0.729901000	-2.069605000	-1.279752000
O	-1.217469000	1.928343000	-0.758064000
O	-3.336899000	1.449448000	-0.163111000
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H	-3.435478000	3.382771000	-0.954714000
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1d-iiii S_0

C	-2.854762000	-1.736525000	1.505167000
C	-1.020749000	-0.691234000	-0.984937000
C	-1.999529000	-1.783240000	2.488485000
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C	3.863211000	-0.940532000	-0.881621000
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H	3.723688000	-1.621223000	-1.714428000
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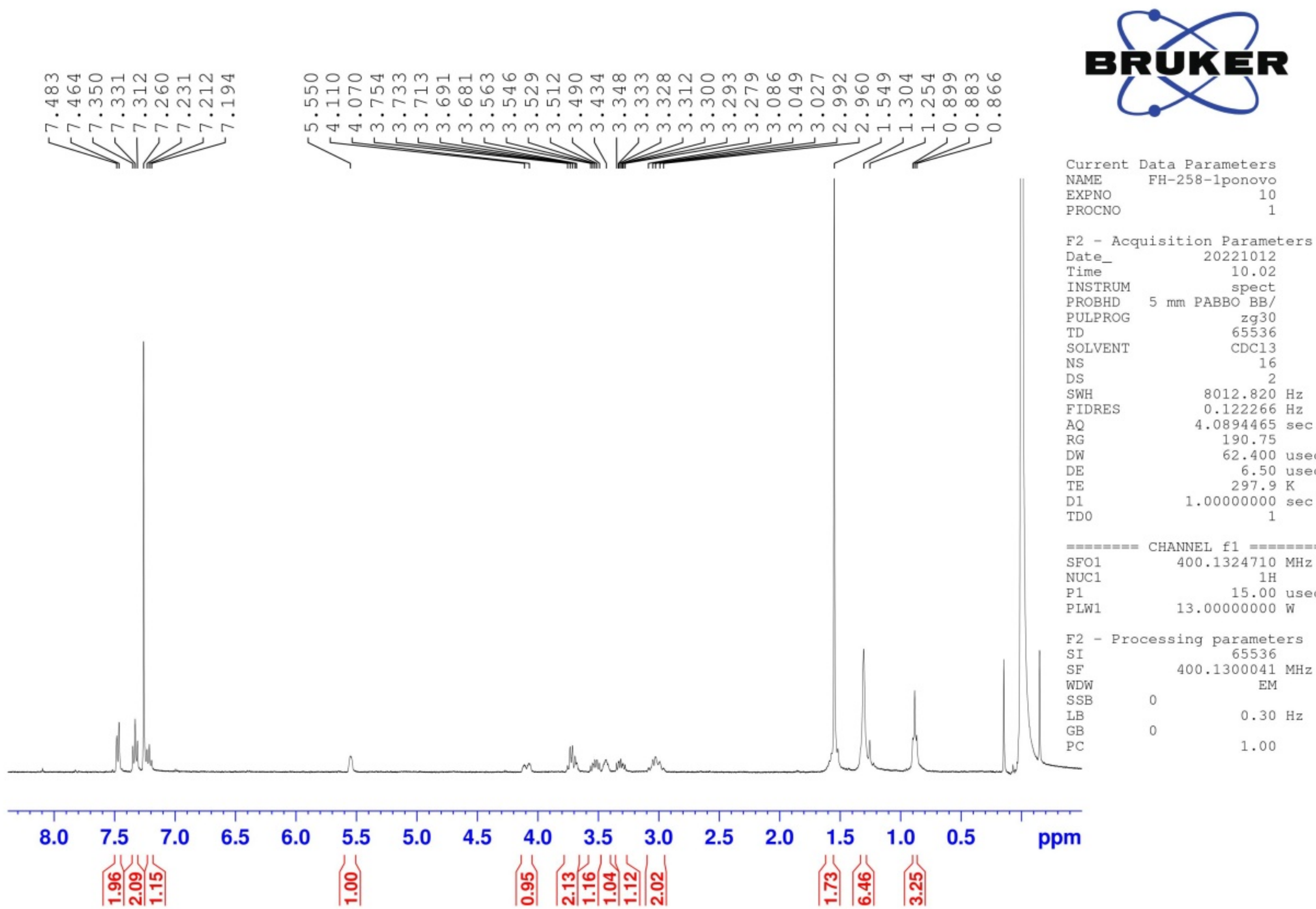
2a ^{1}H NMR spectrum (400 MHz, $CDCl_3$):



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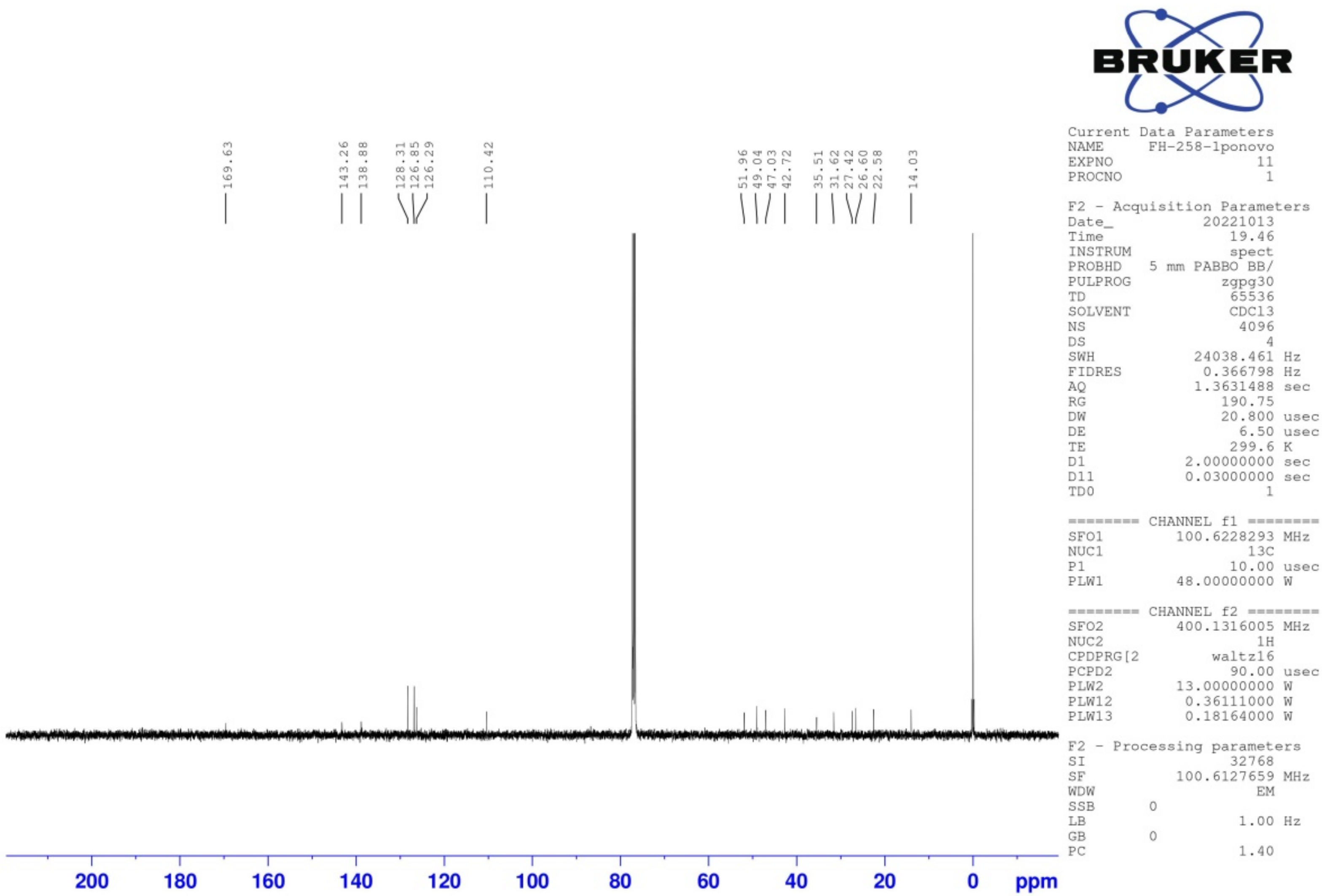

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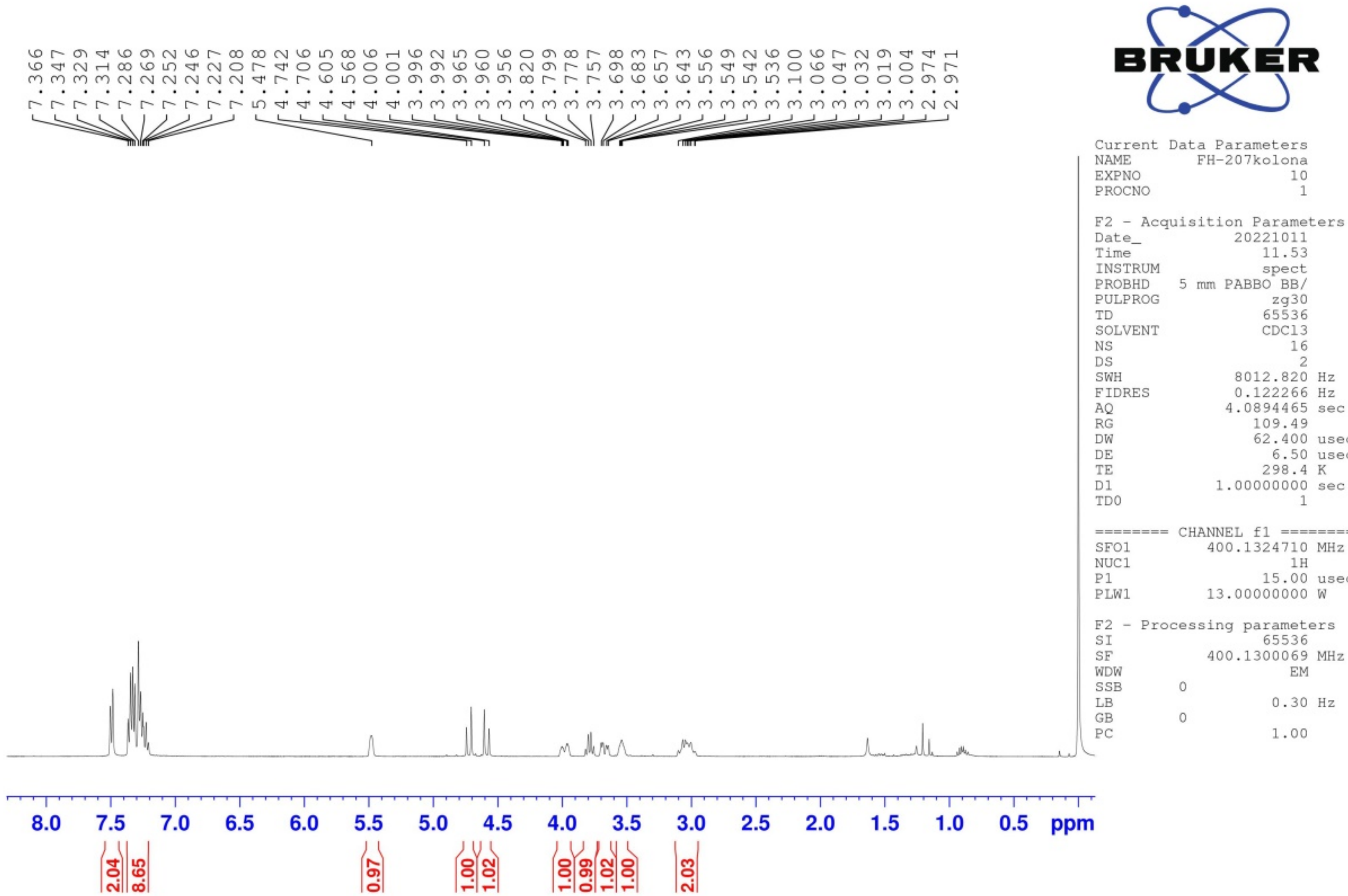

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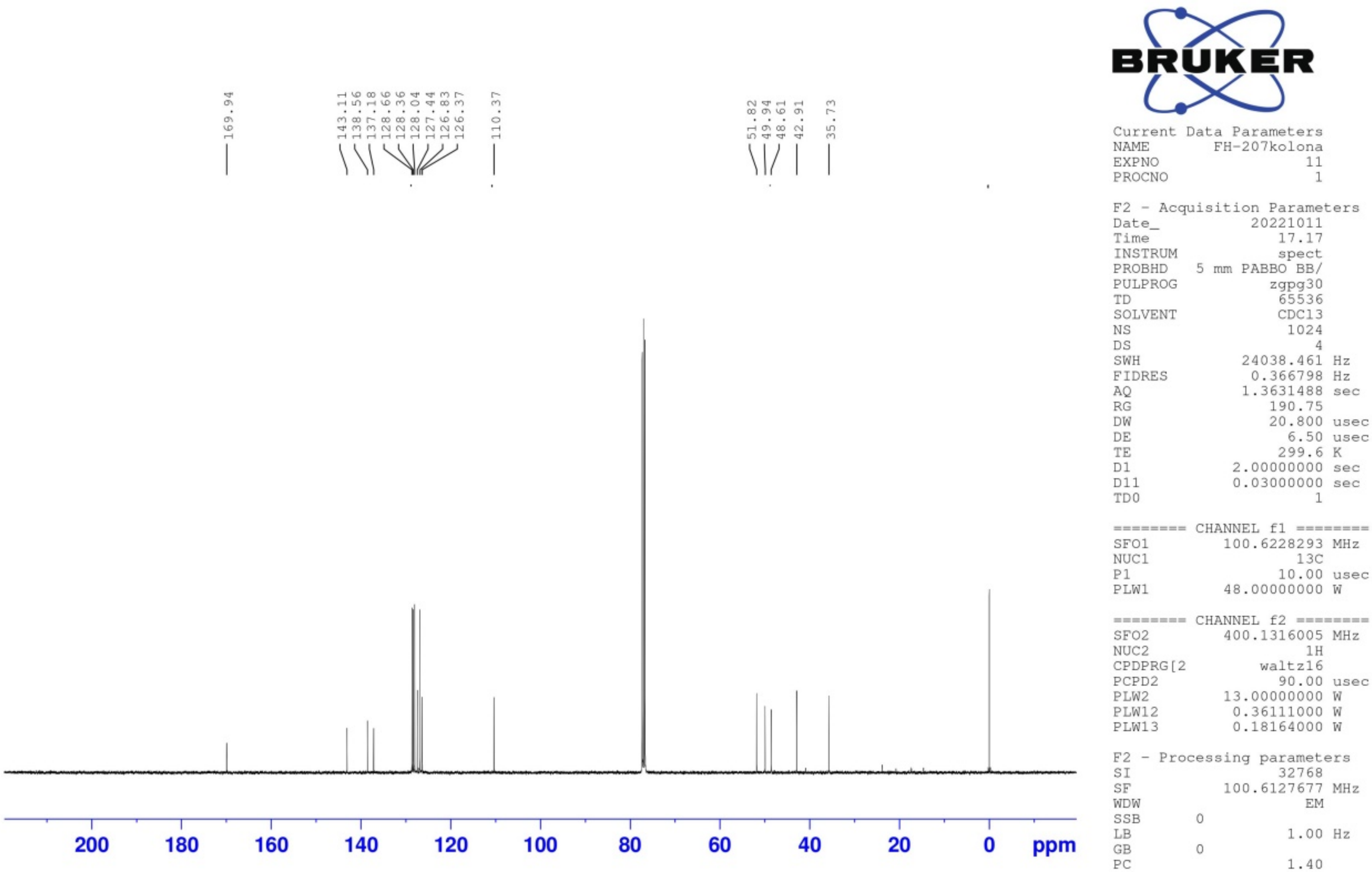

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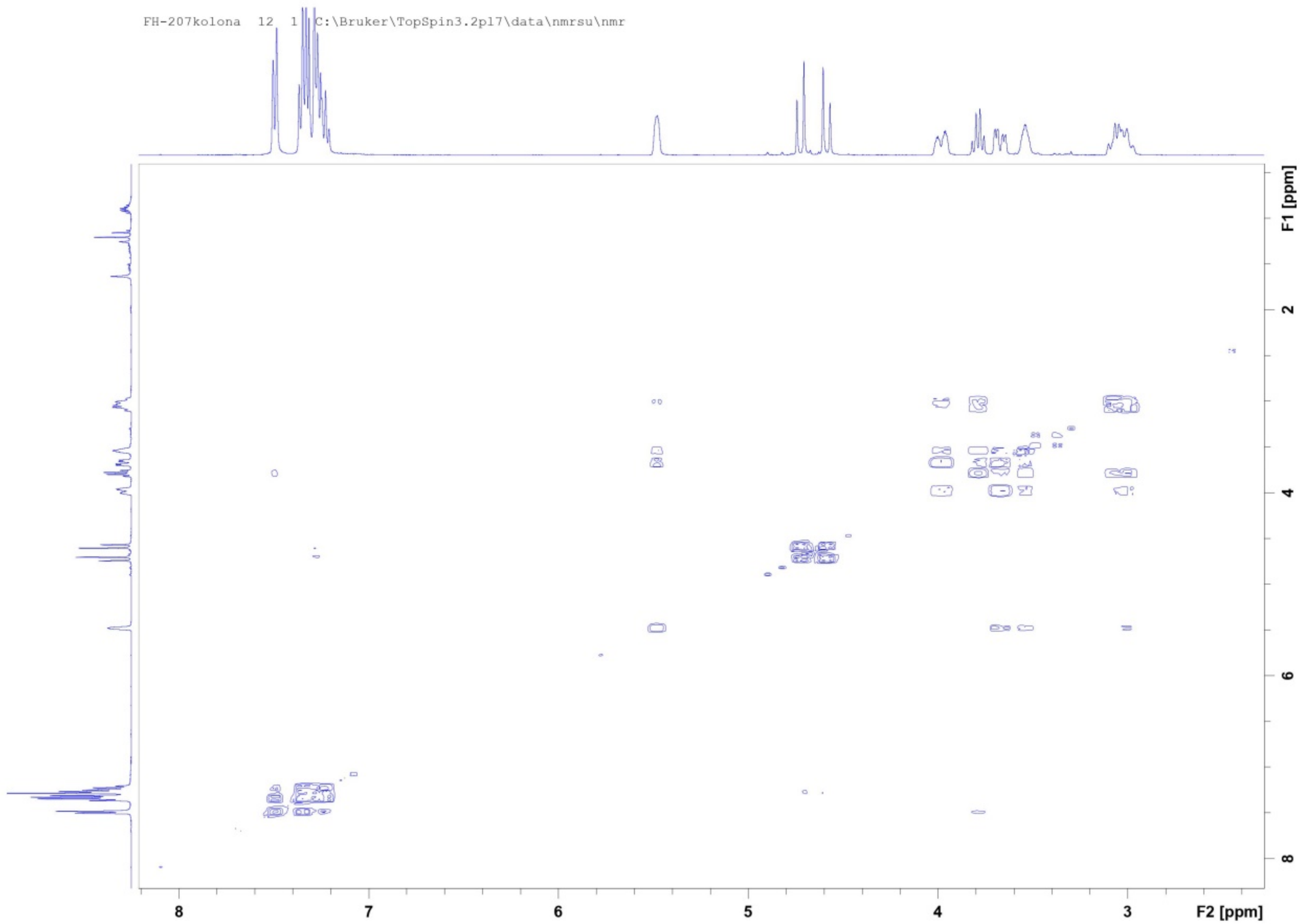

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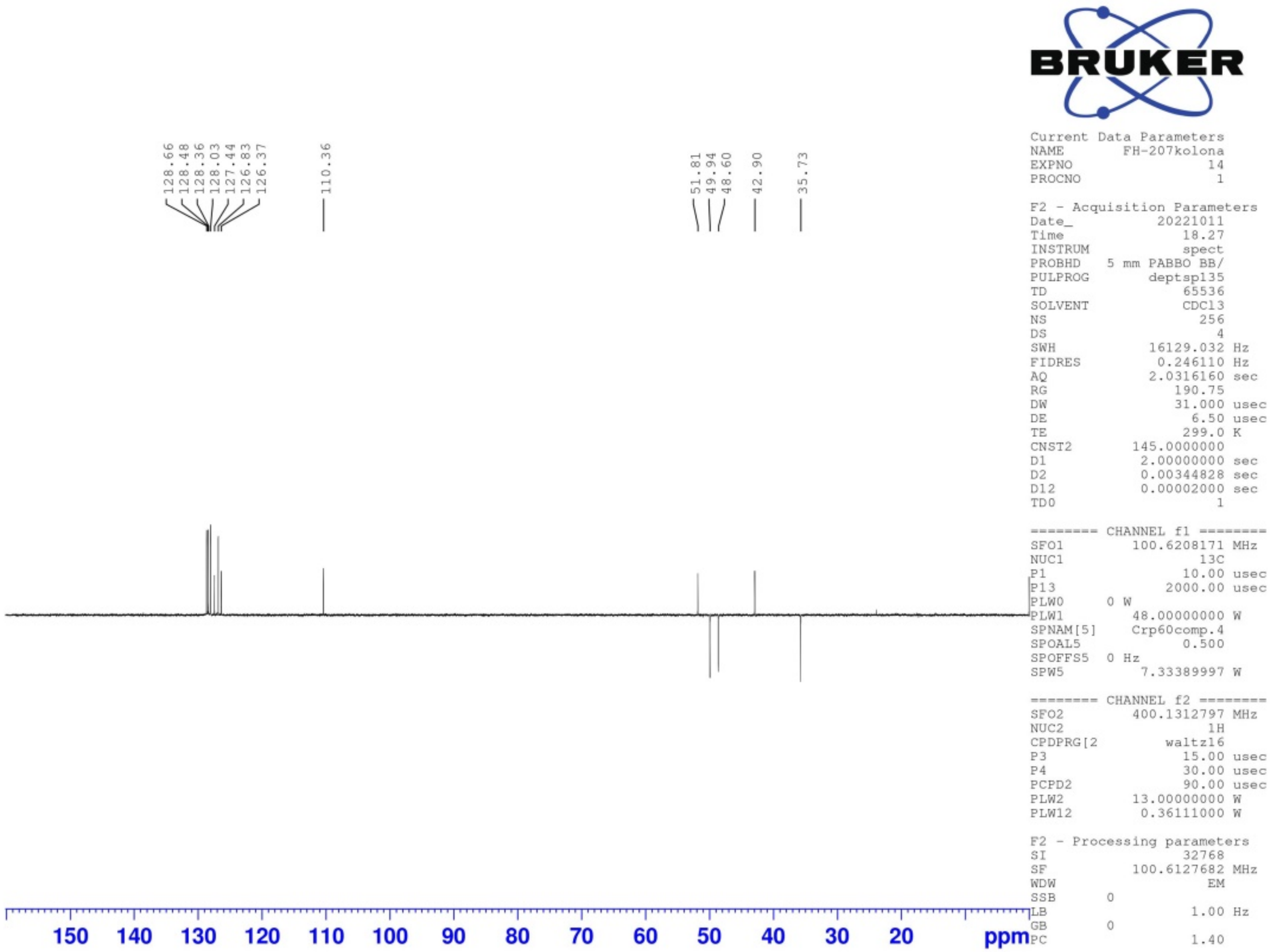

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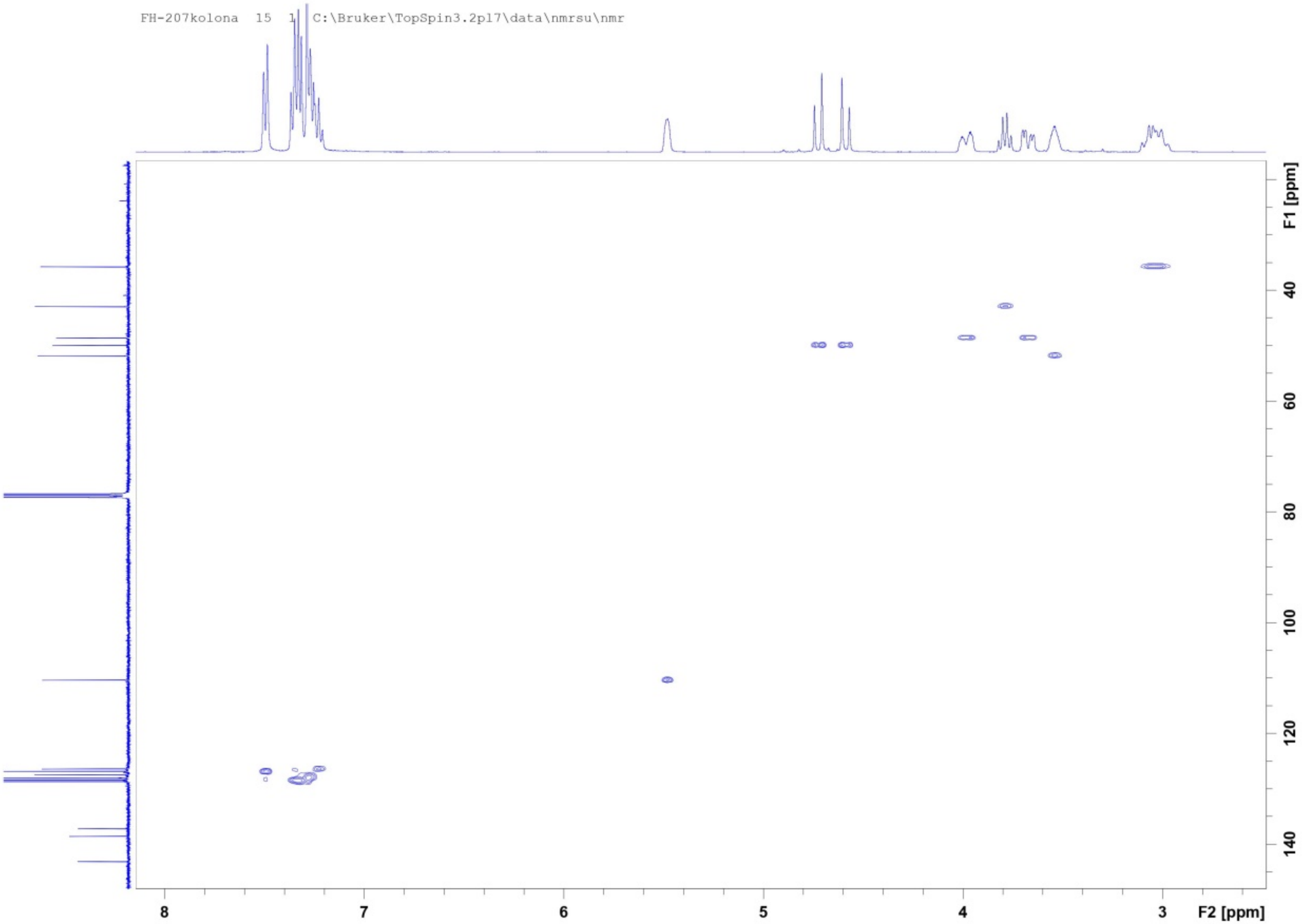

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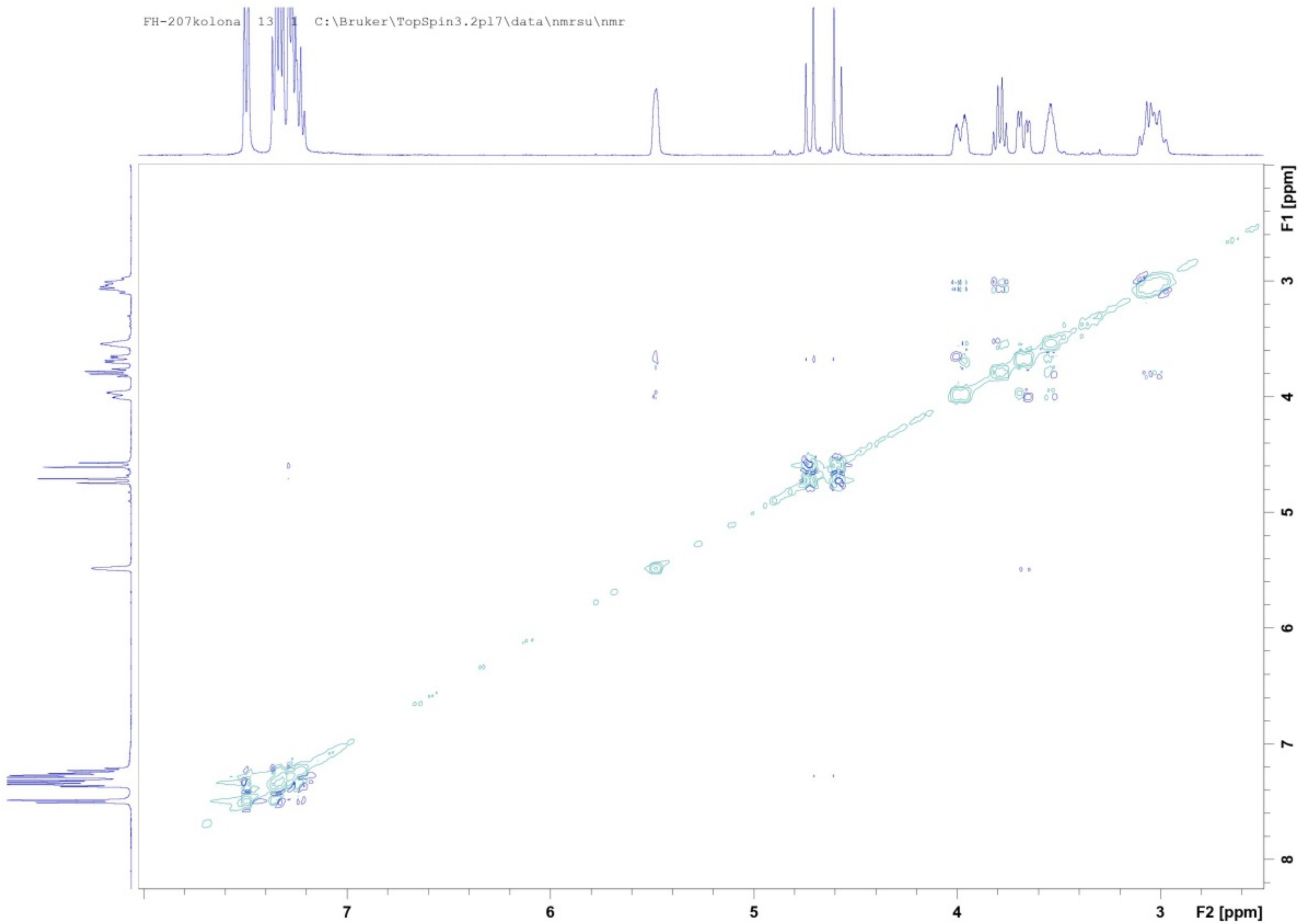

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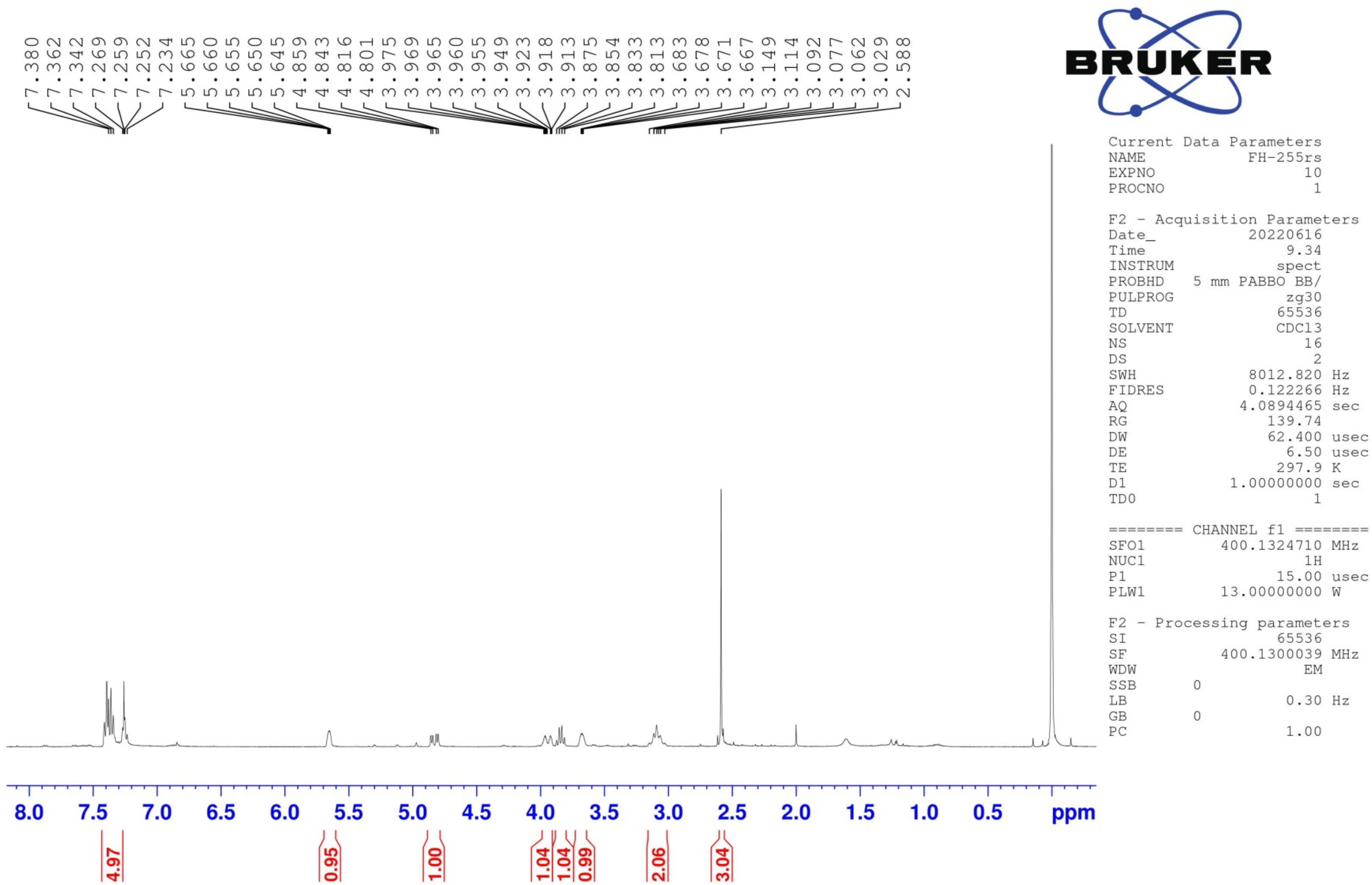

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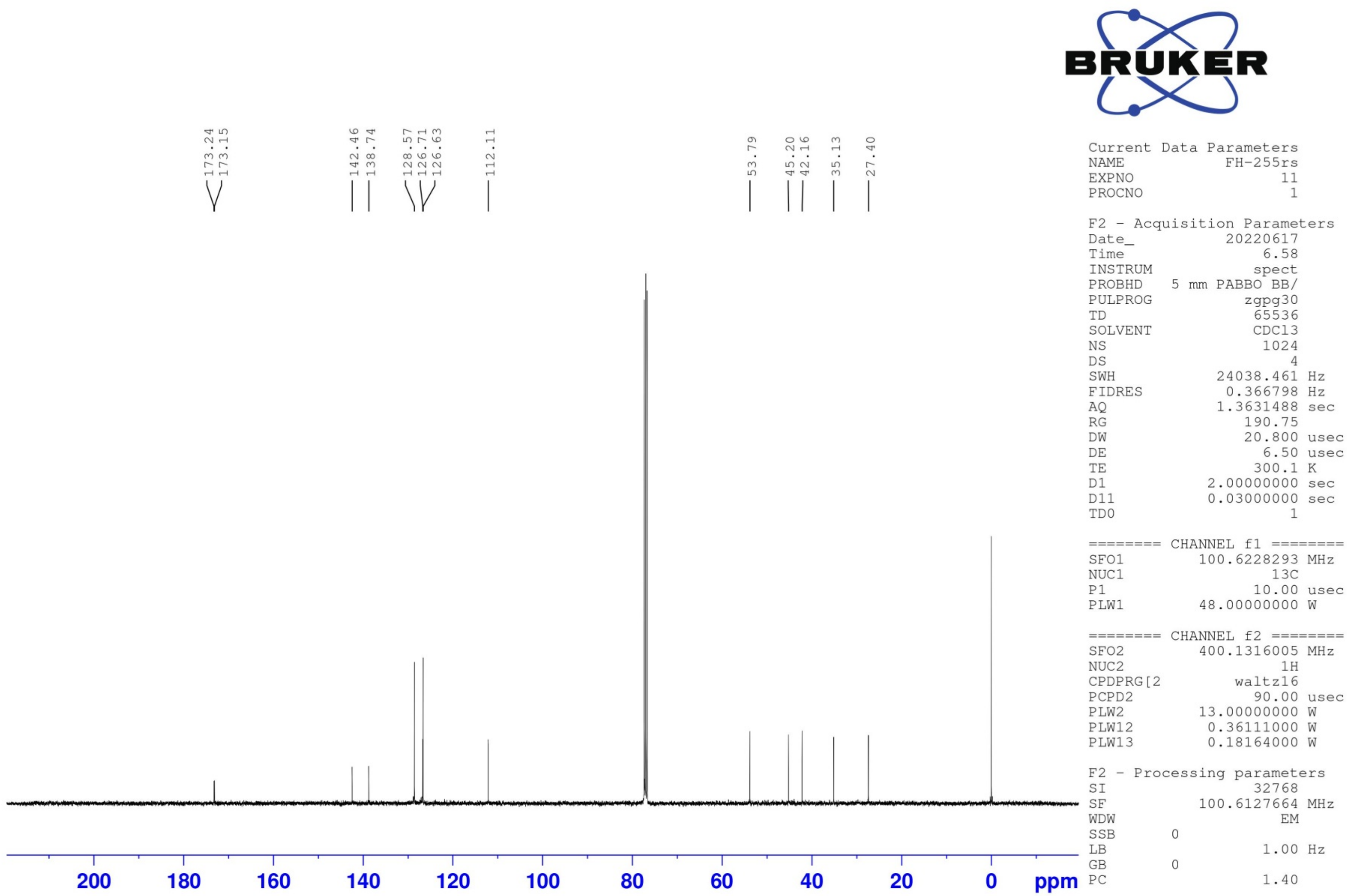

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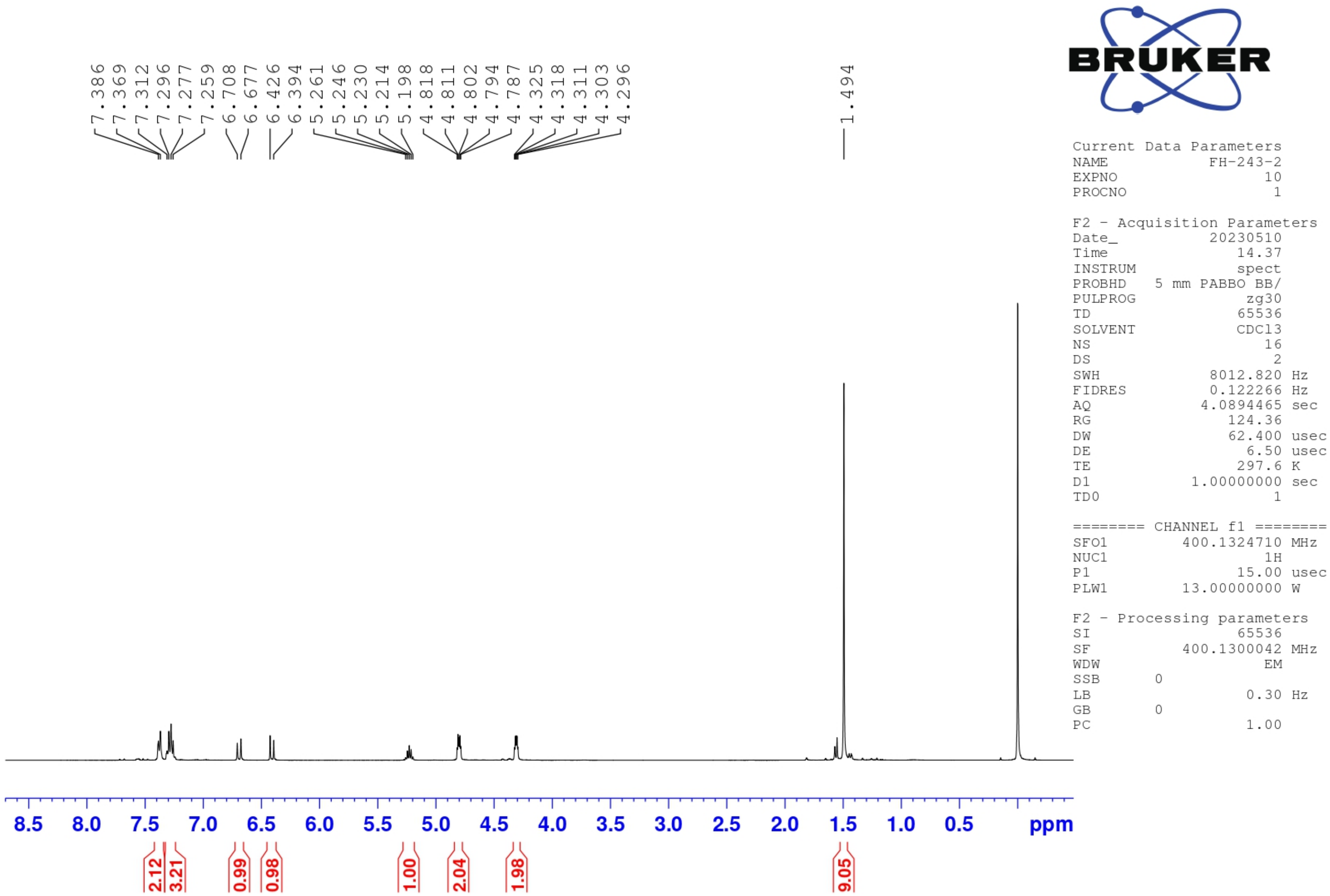

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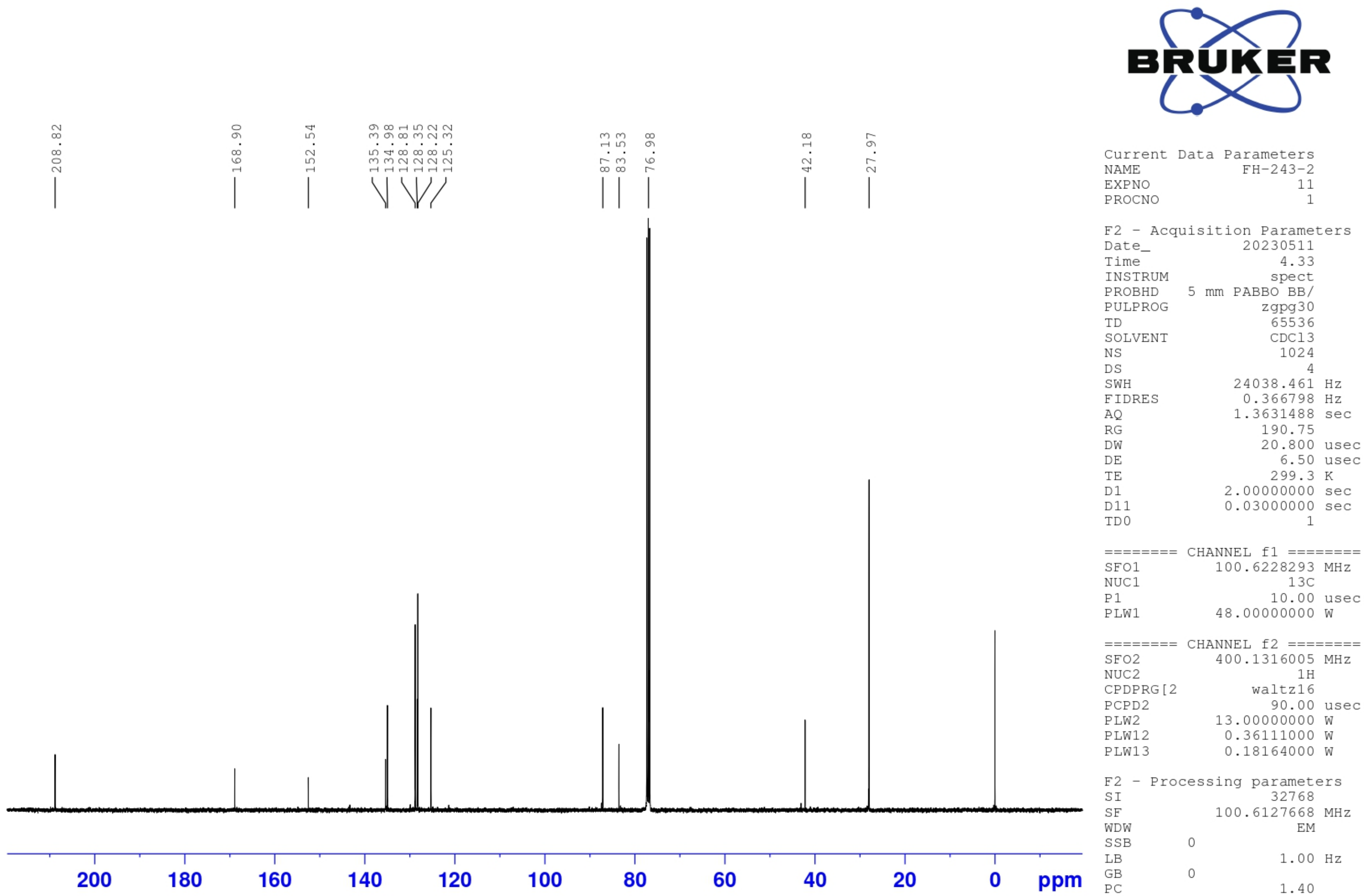

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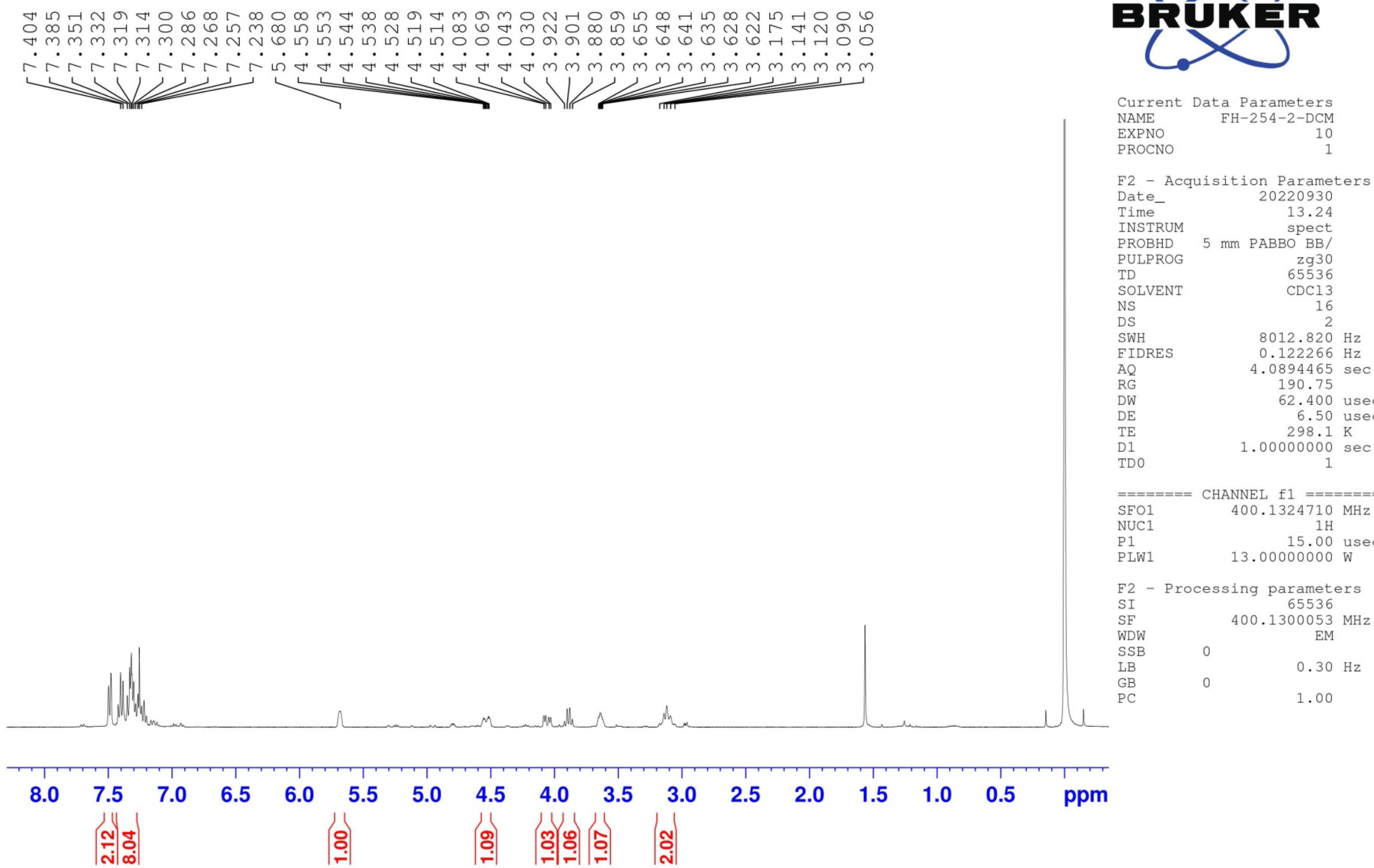

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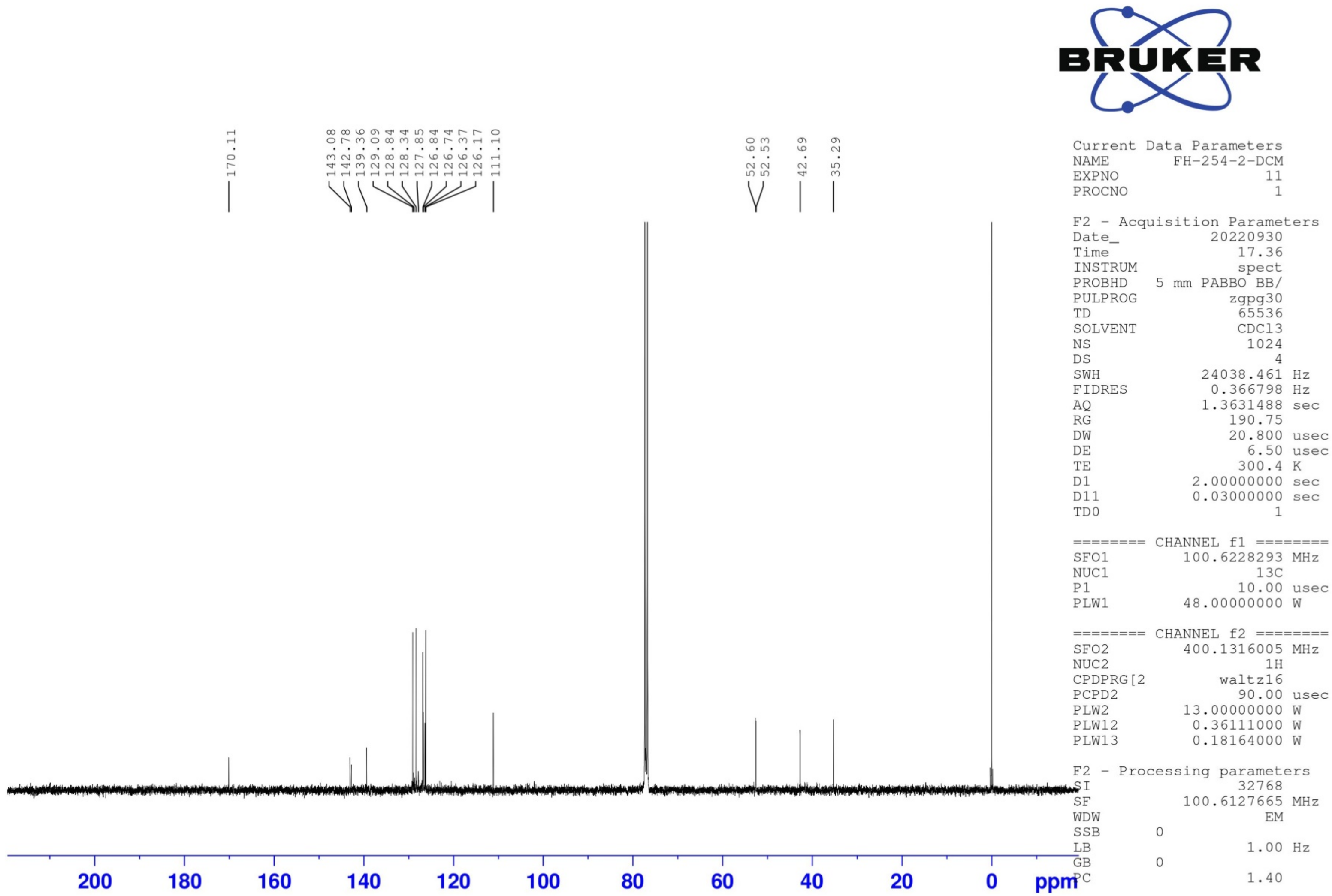

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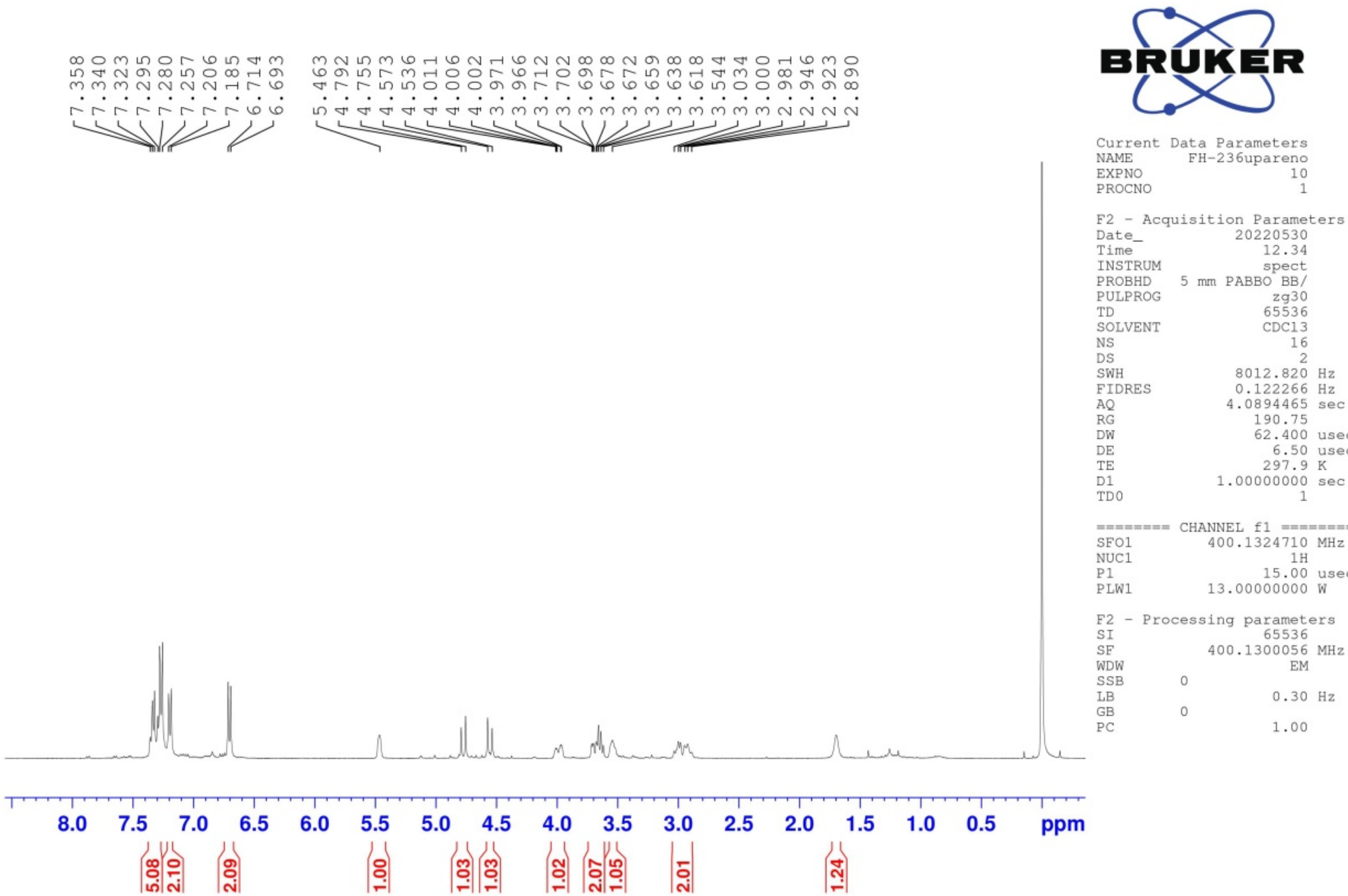

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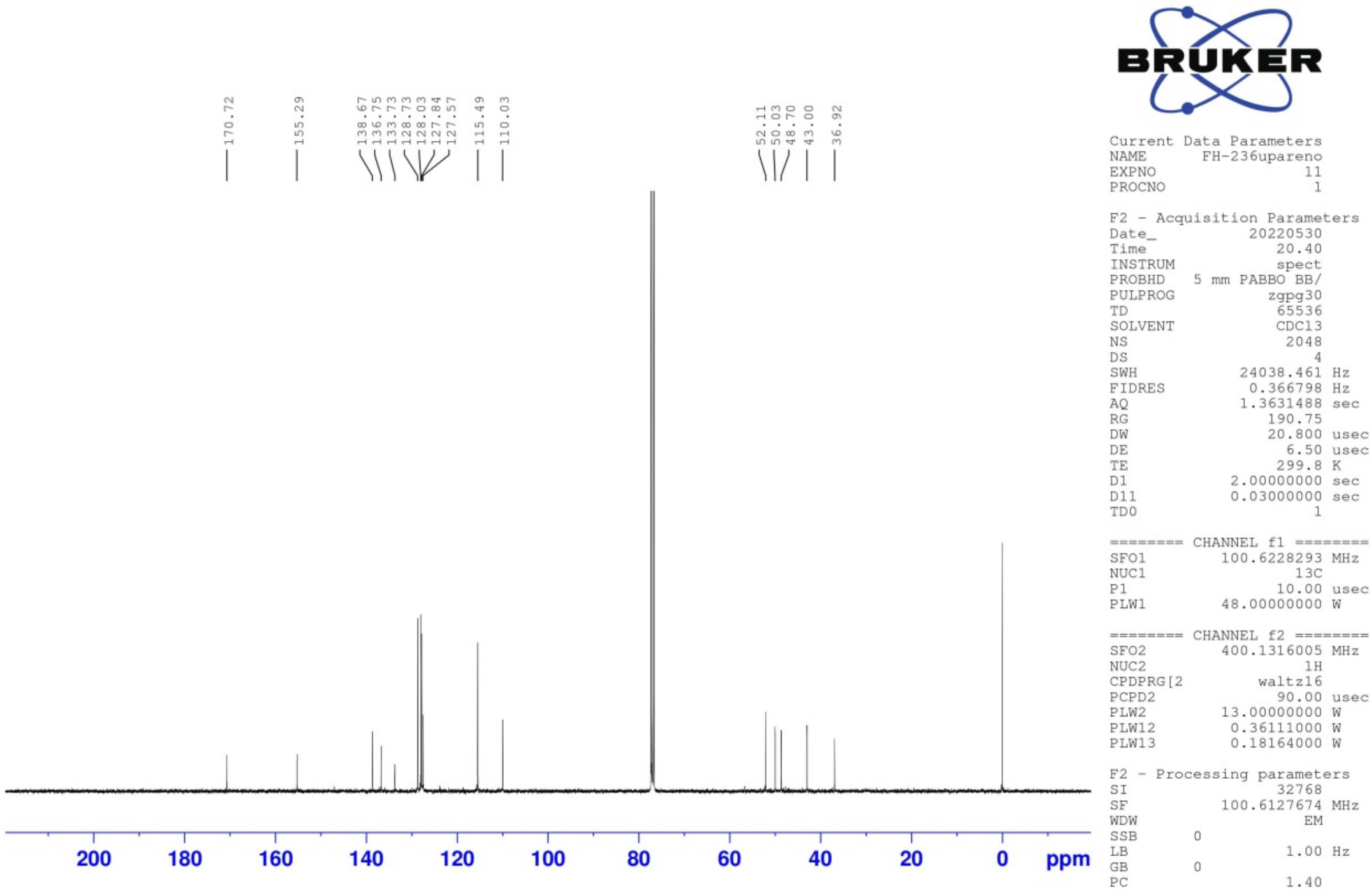

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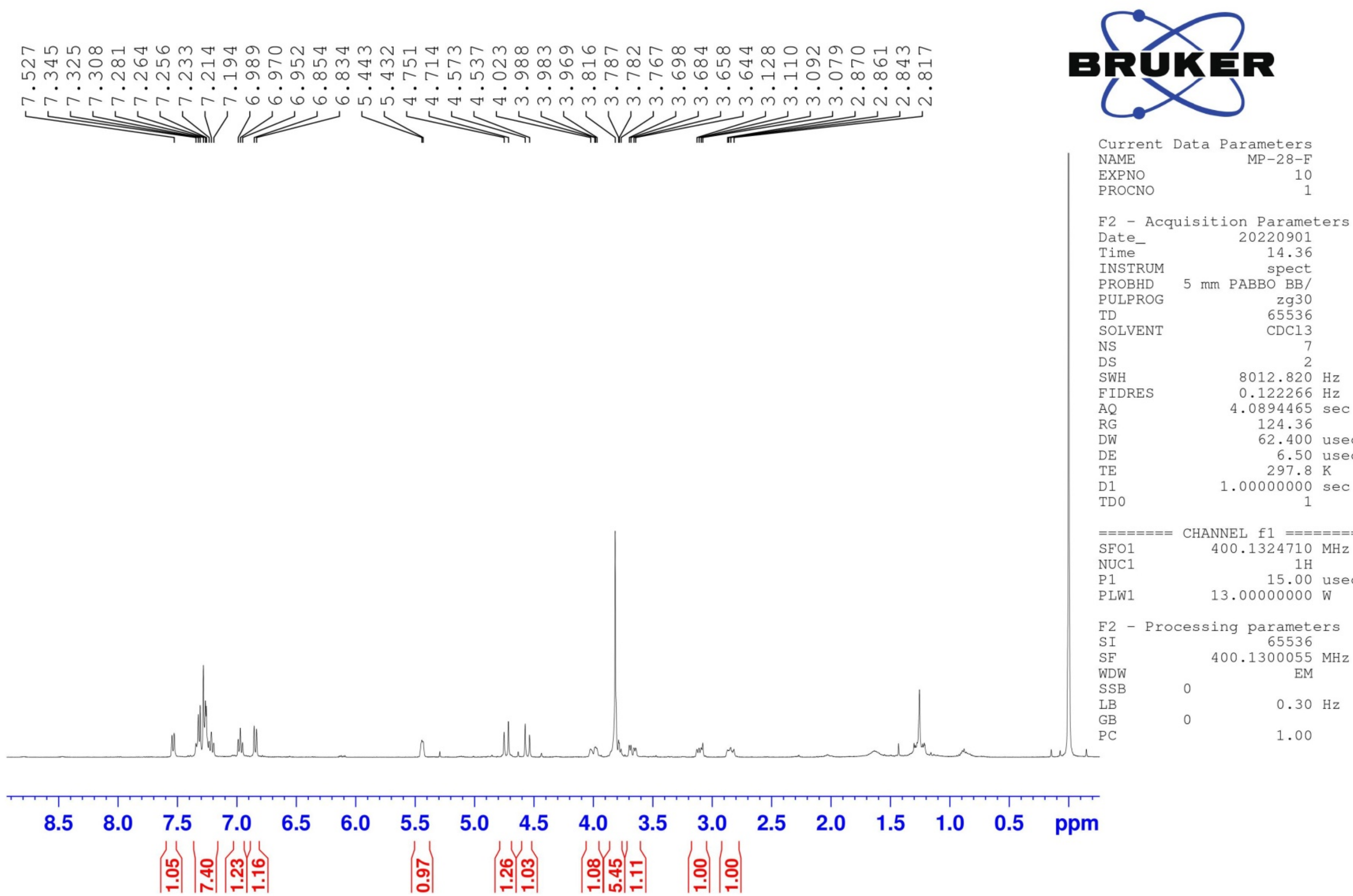

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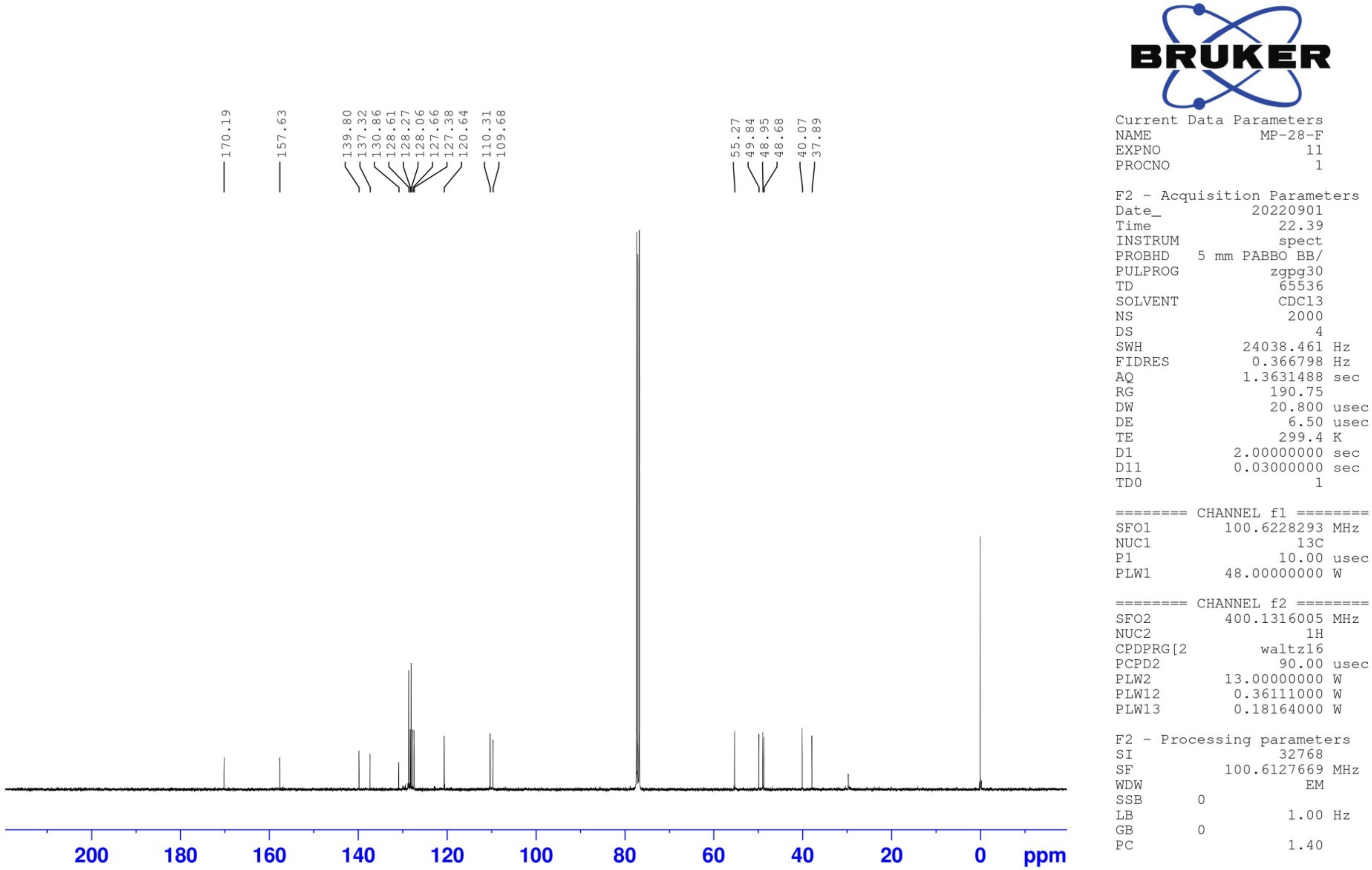

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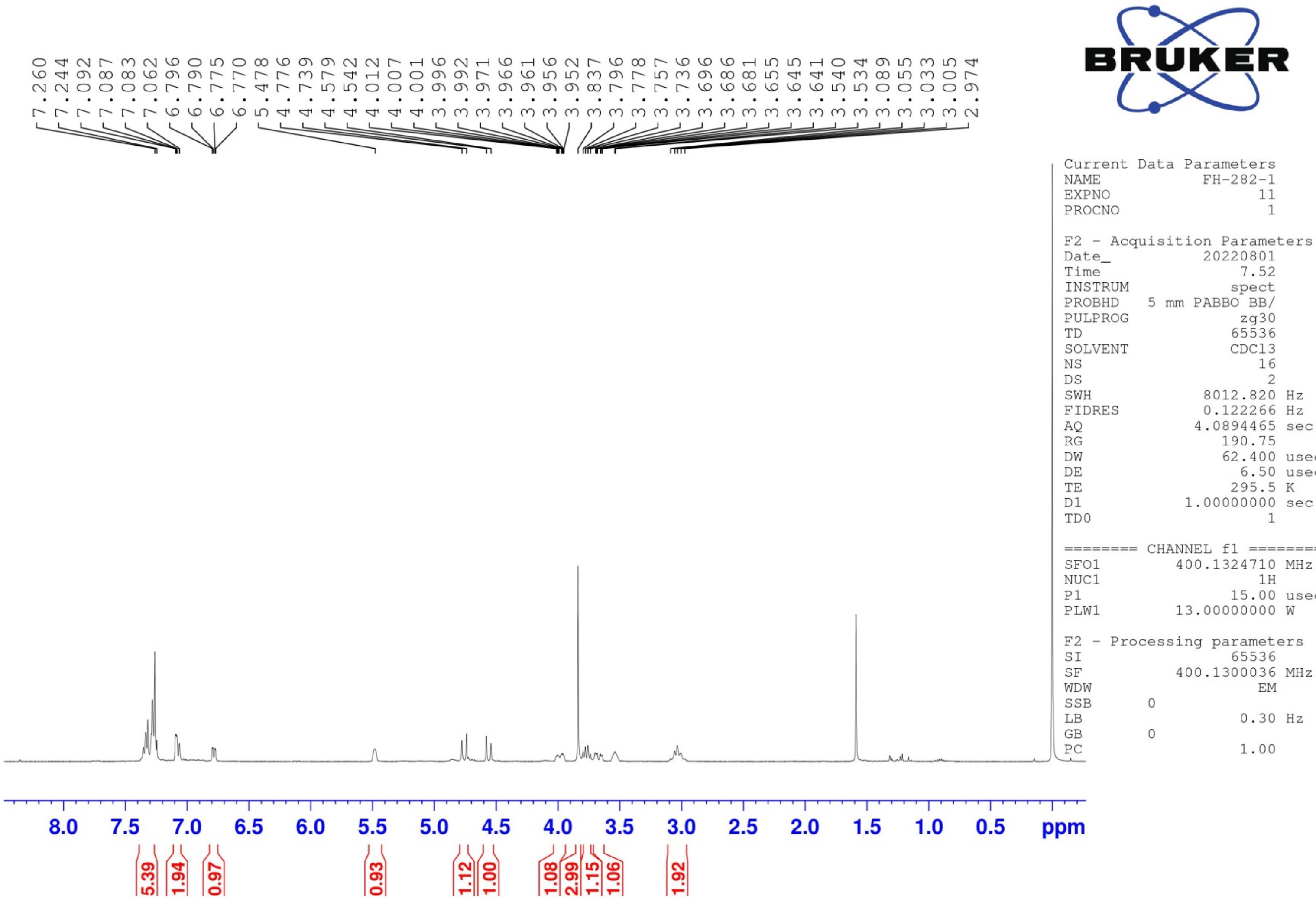

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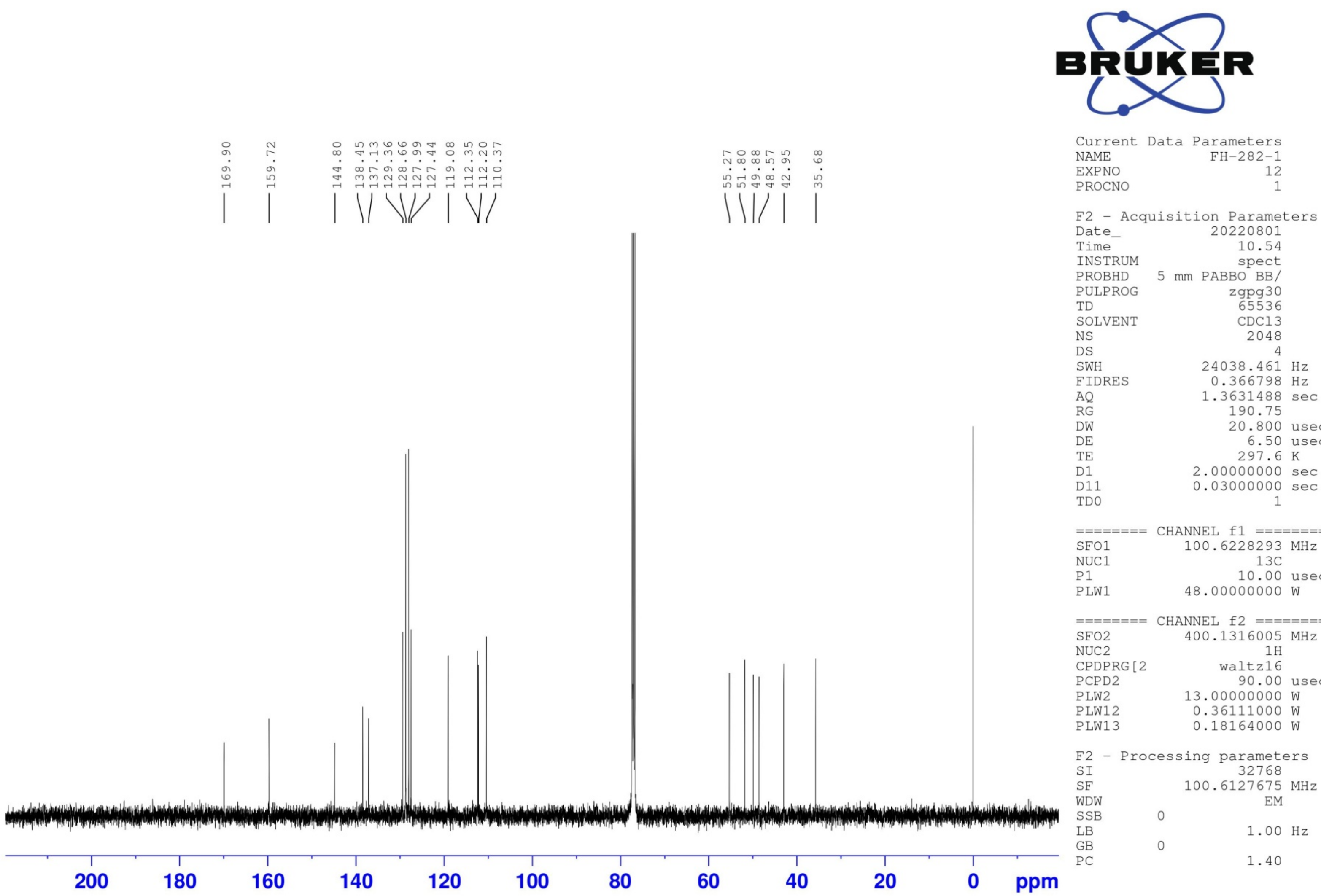

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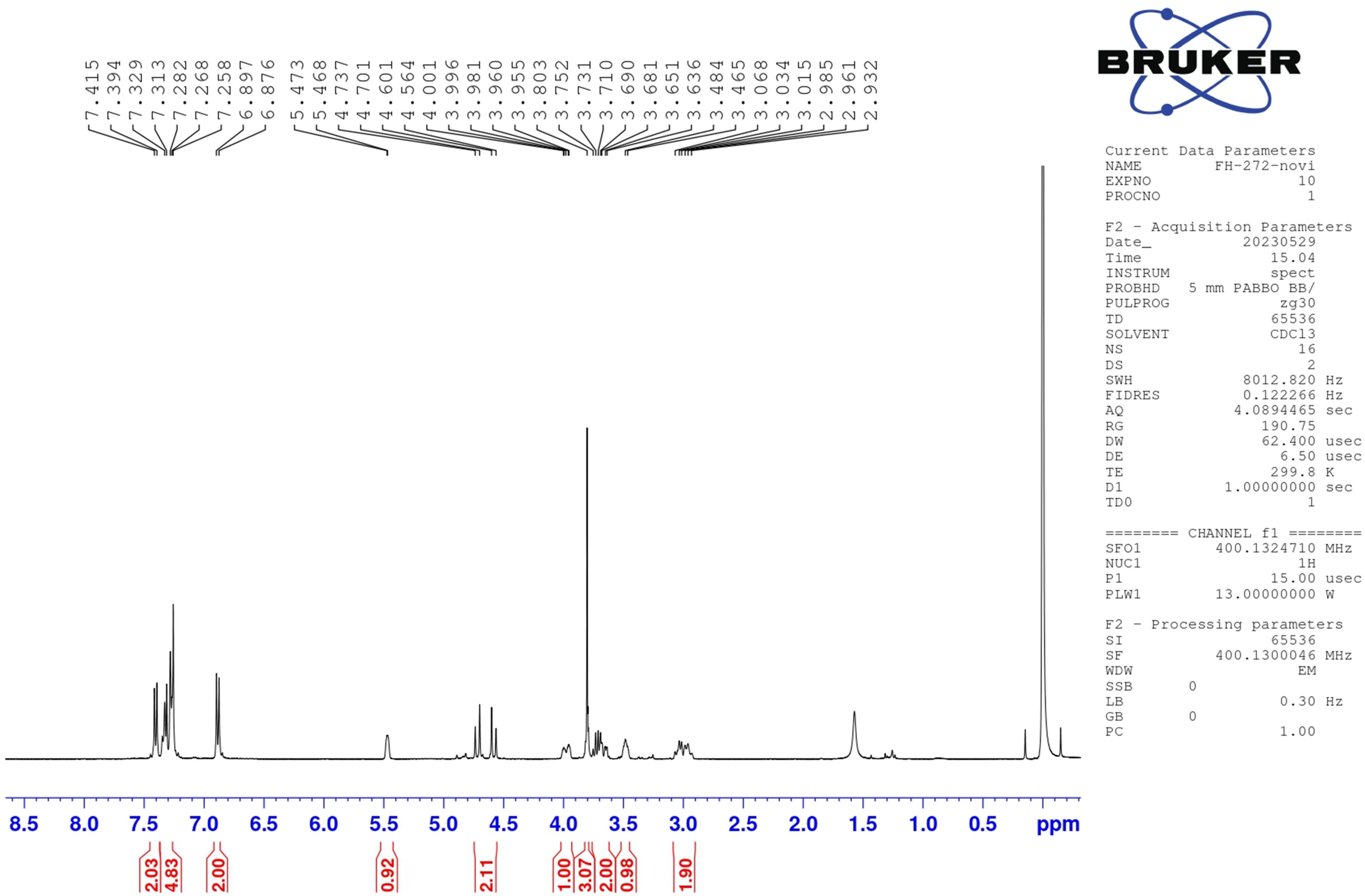

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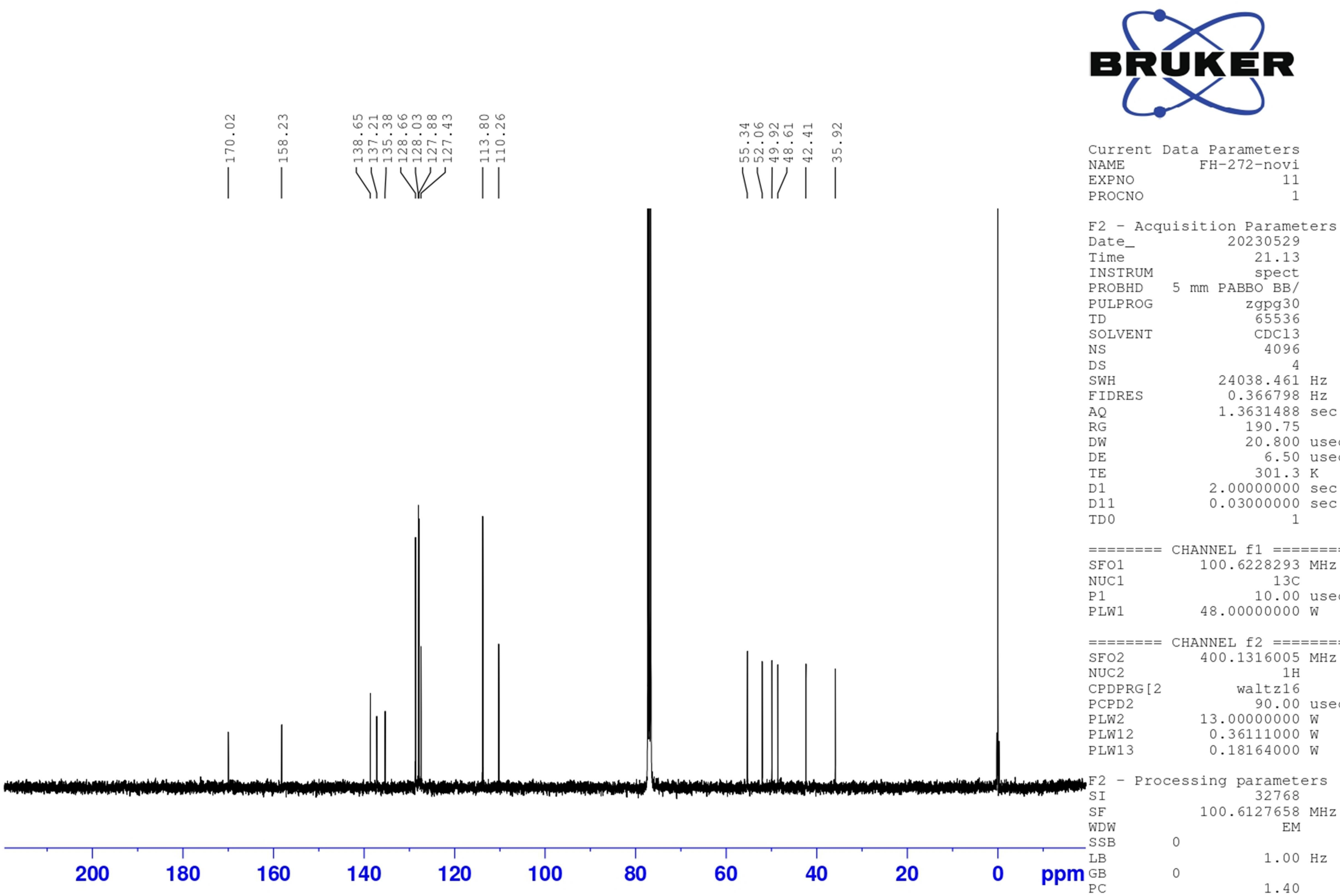

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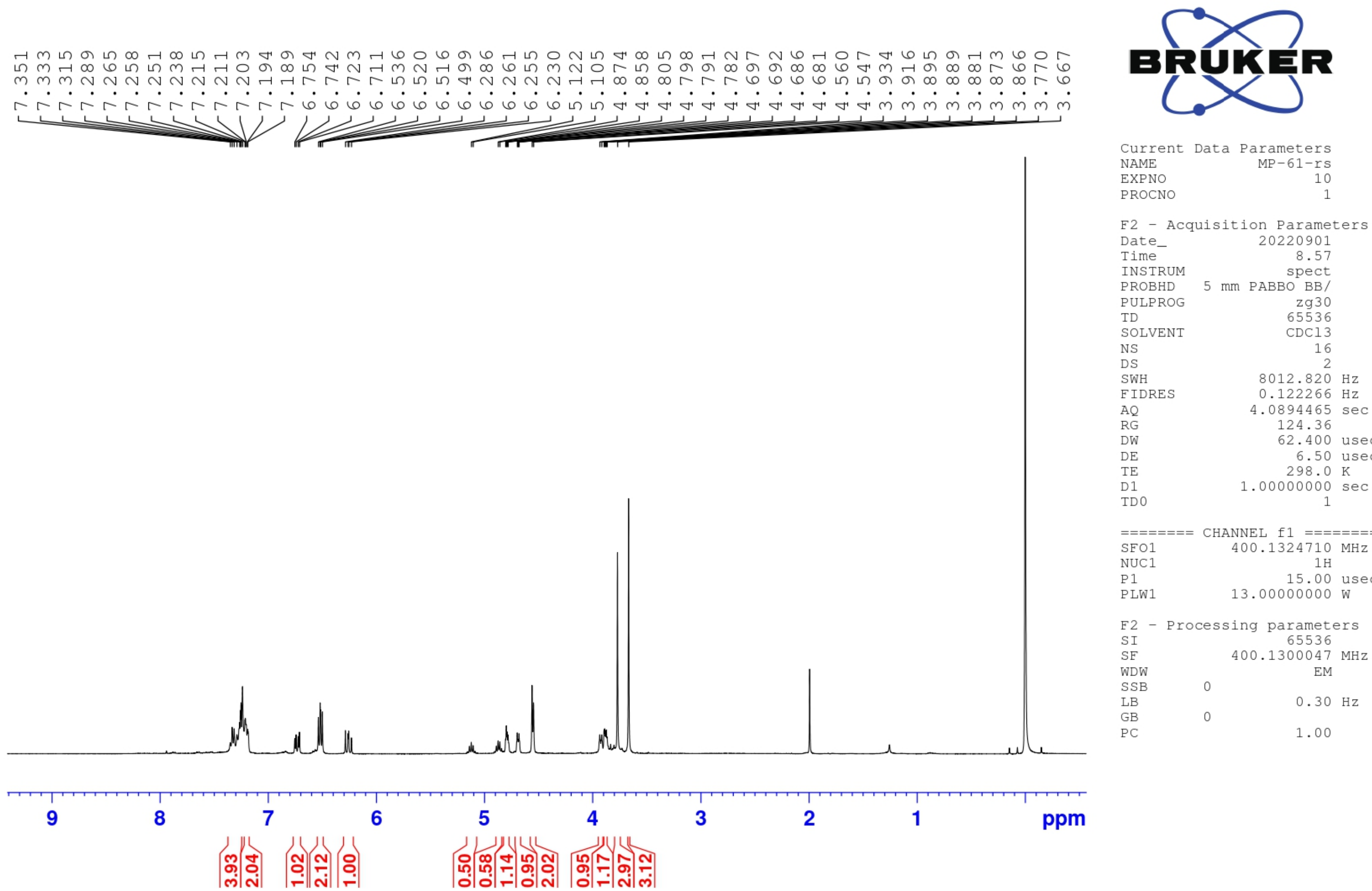

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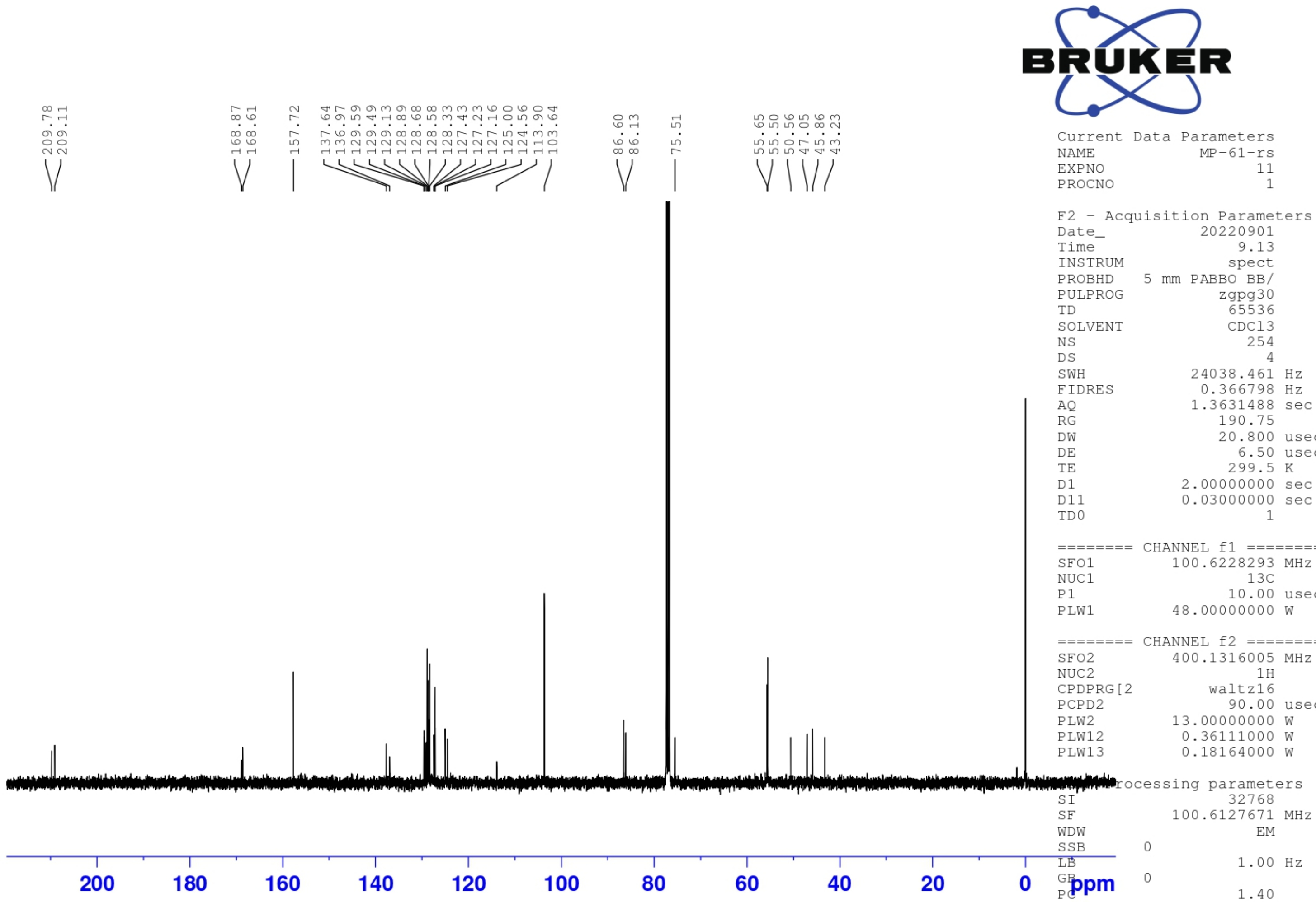

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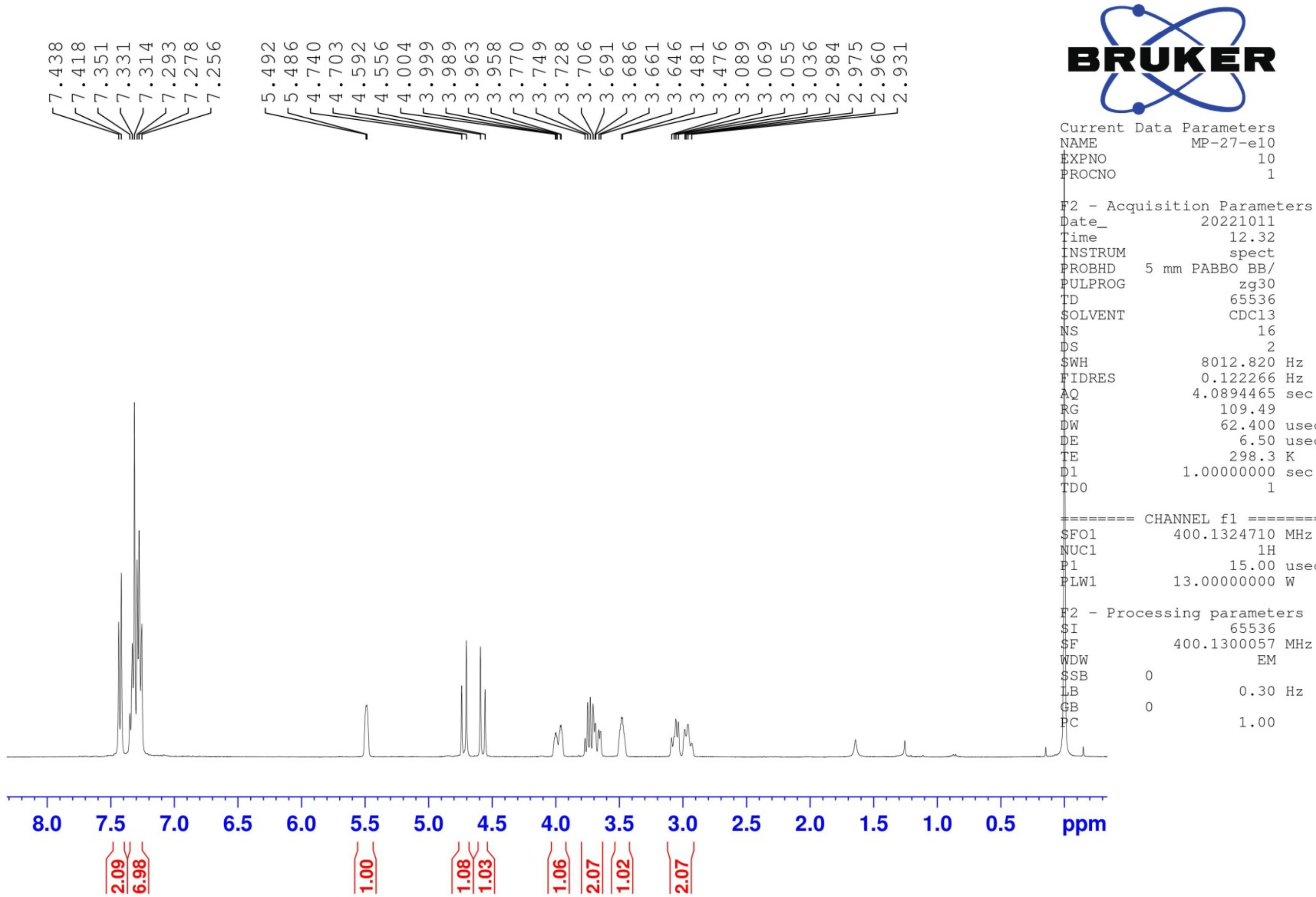

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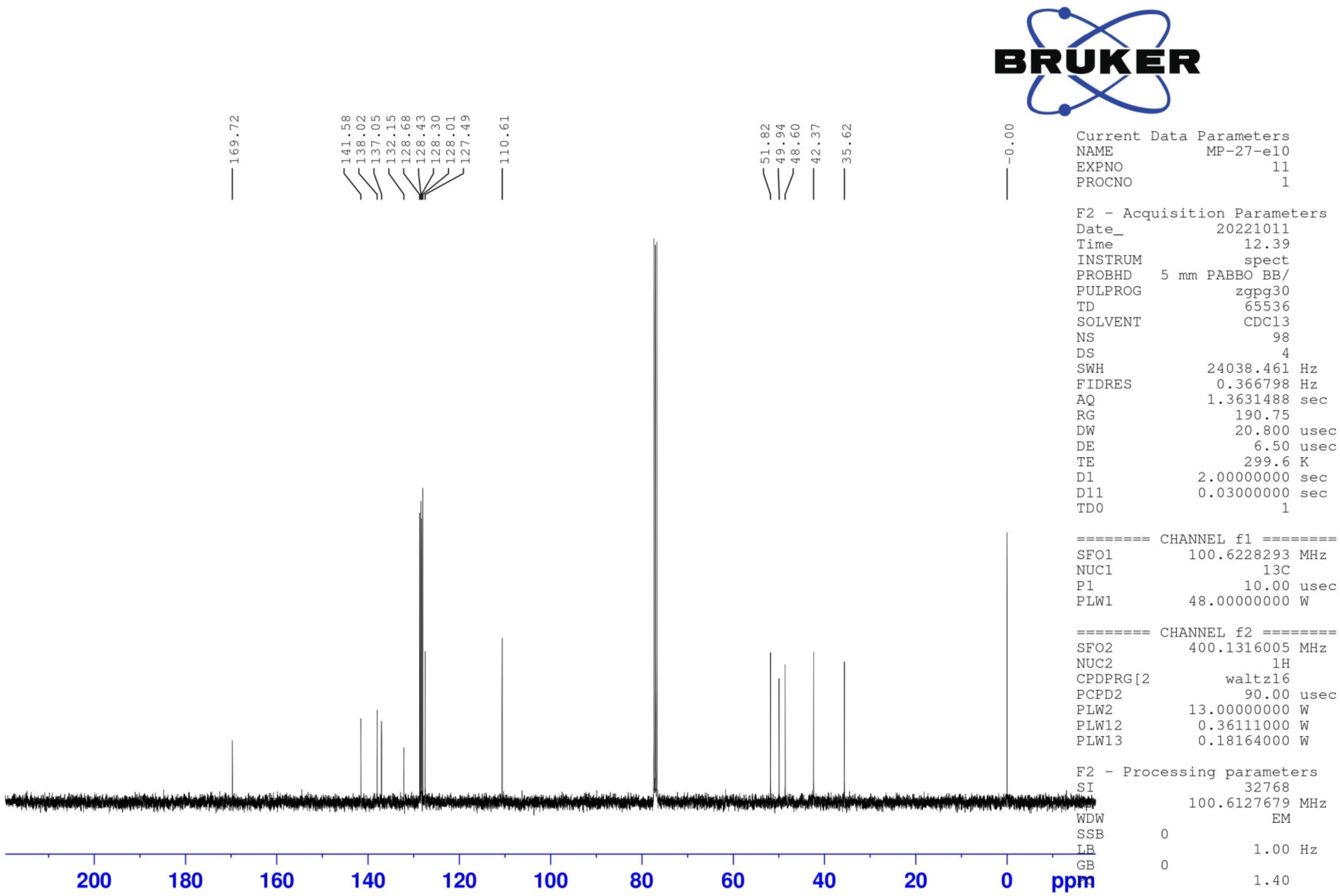

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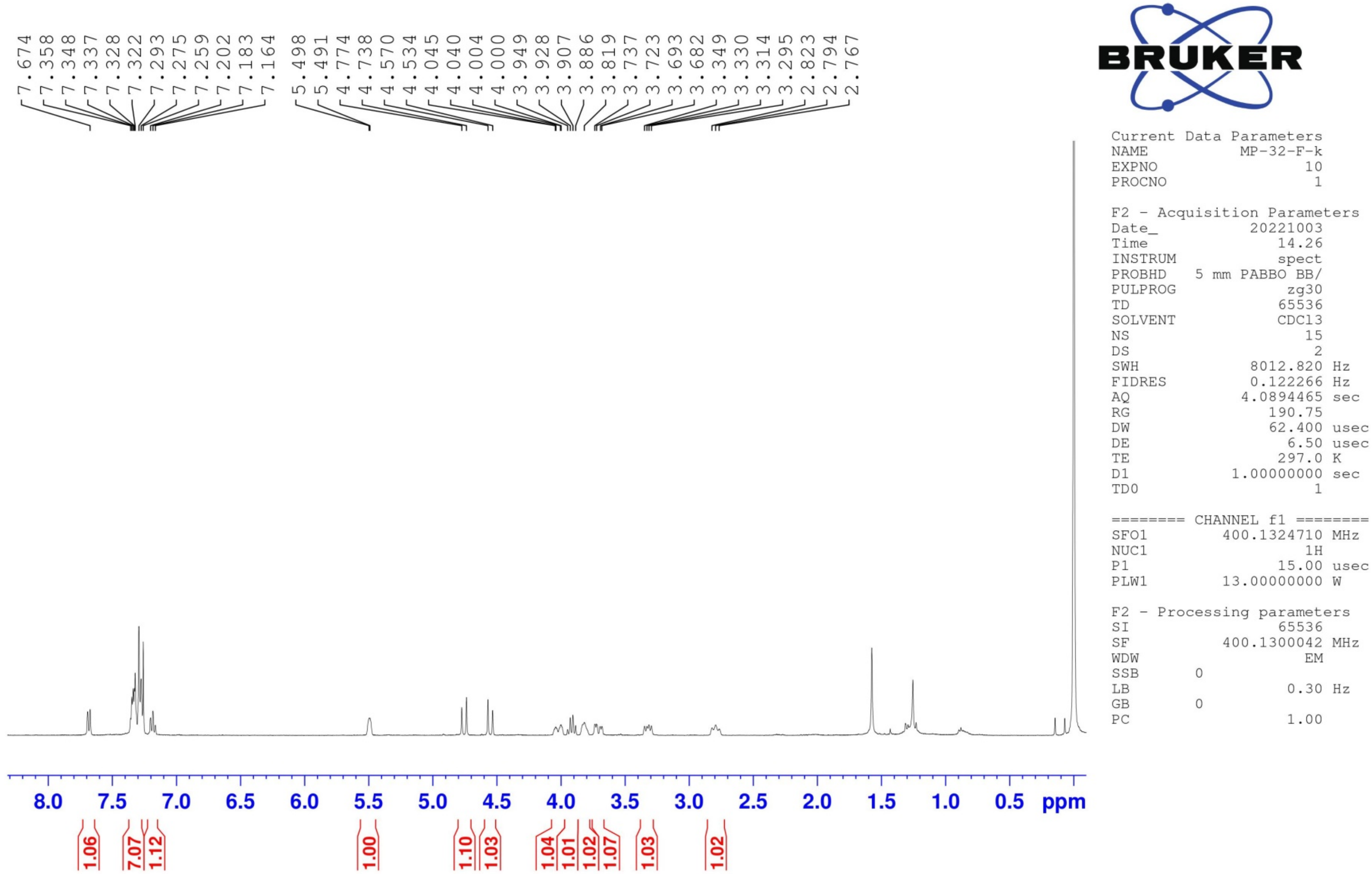

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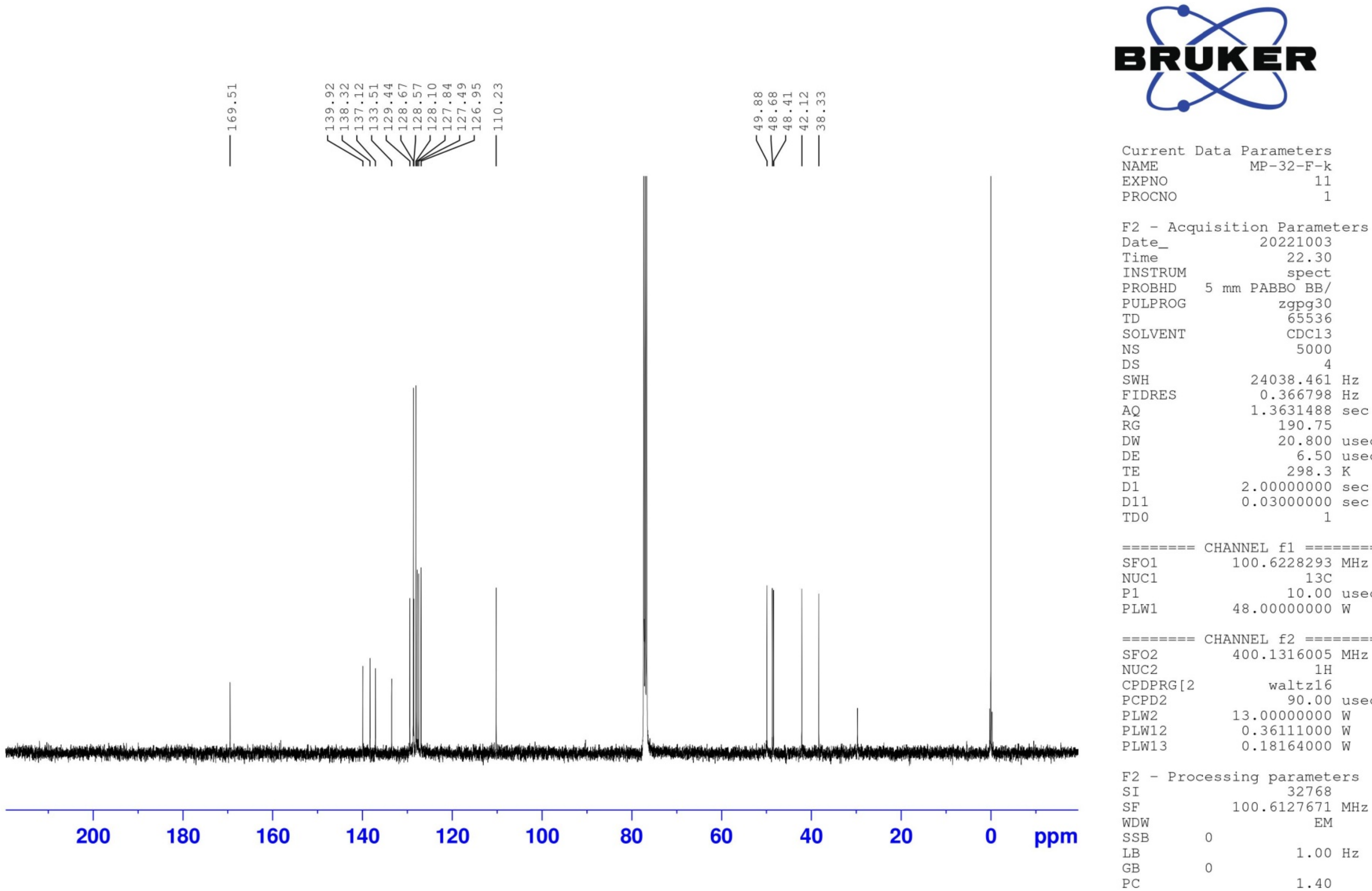

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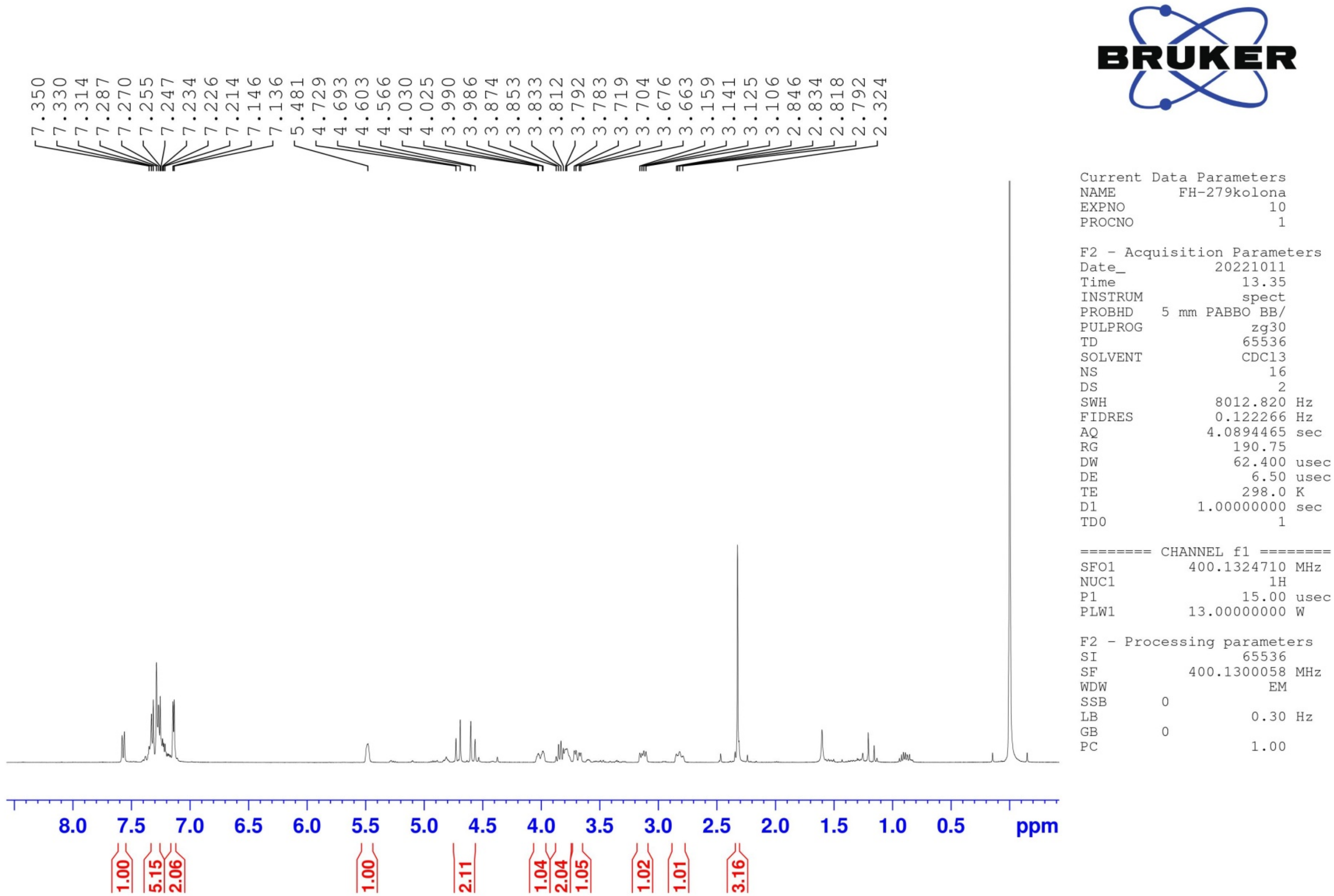

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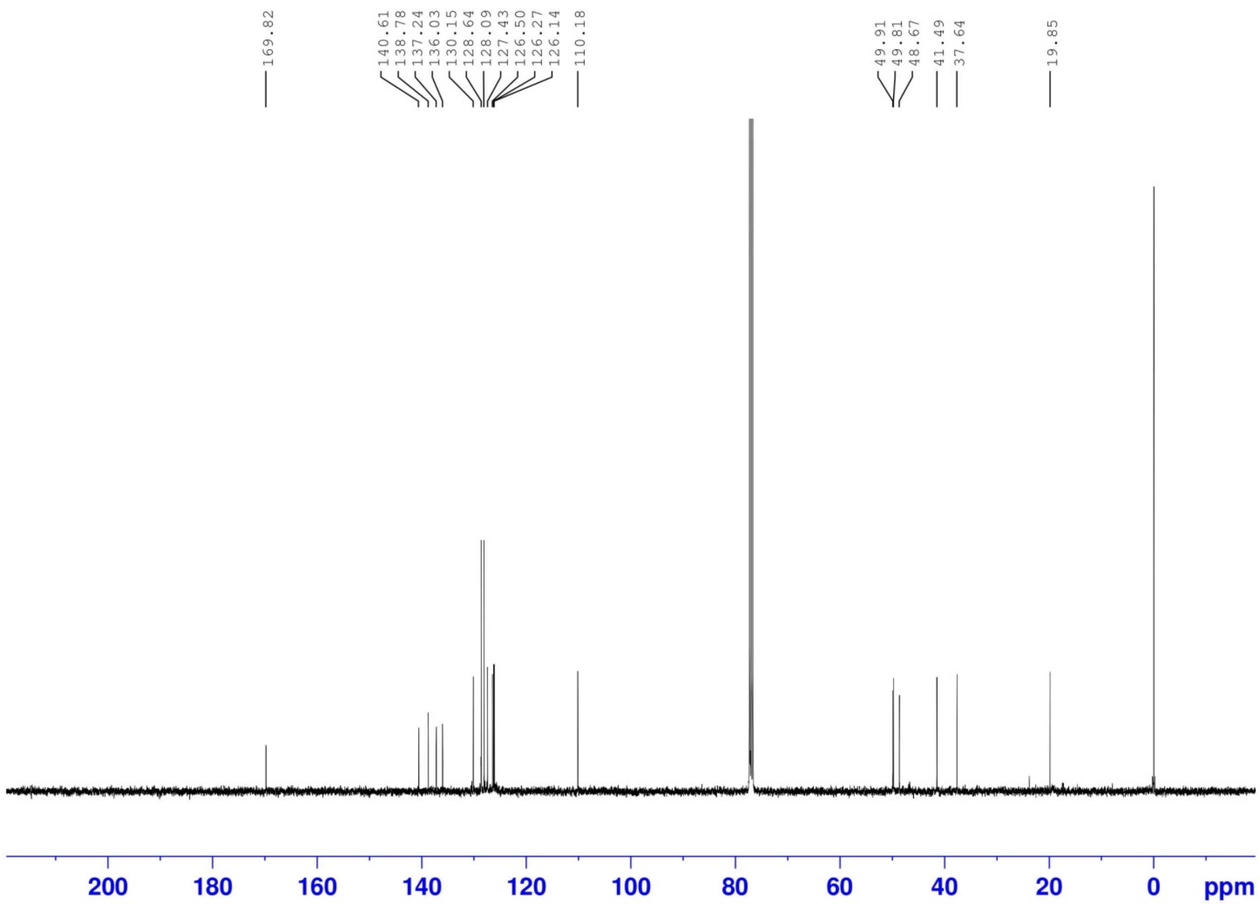


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Date_           20221011
Time               19.44
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG               190.75
DW               20.800 usec
DE                 6.50 usec
TE                299.7 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1                 13C
P1                 10.00 usec
PLW1        48.00000000 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2        13.00000000 W
PLW12        0.36111000 W
PLW13        0.18164000 W

F2 - Processing parameters
SI                 32768
SF          100.6127672 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
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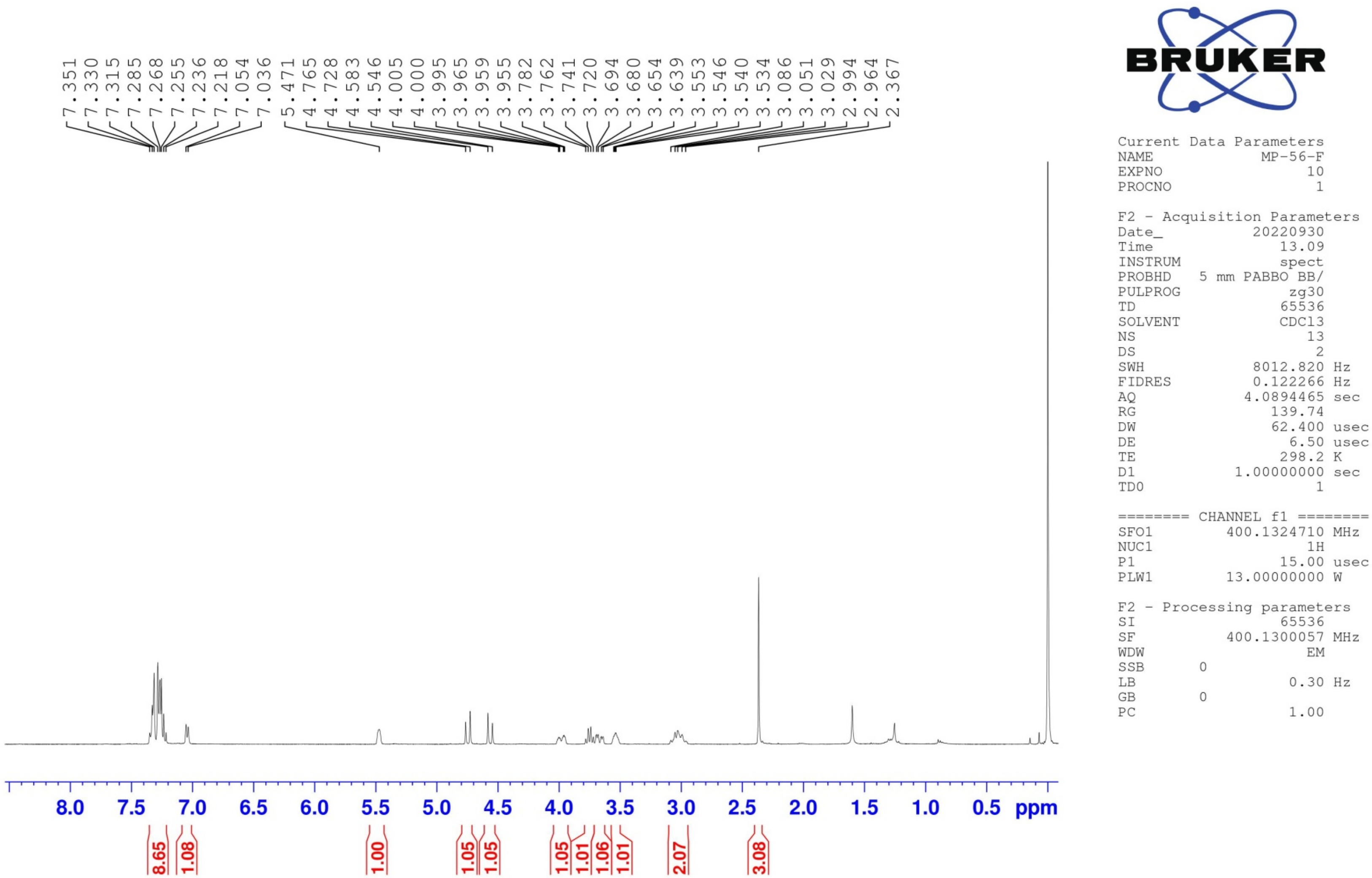
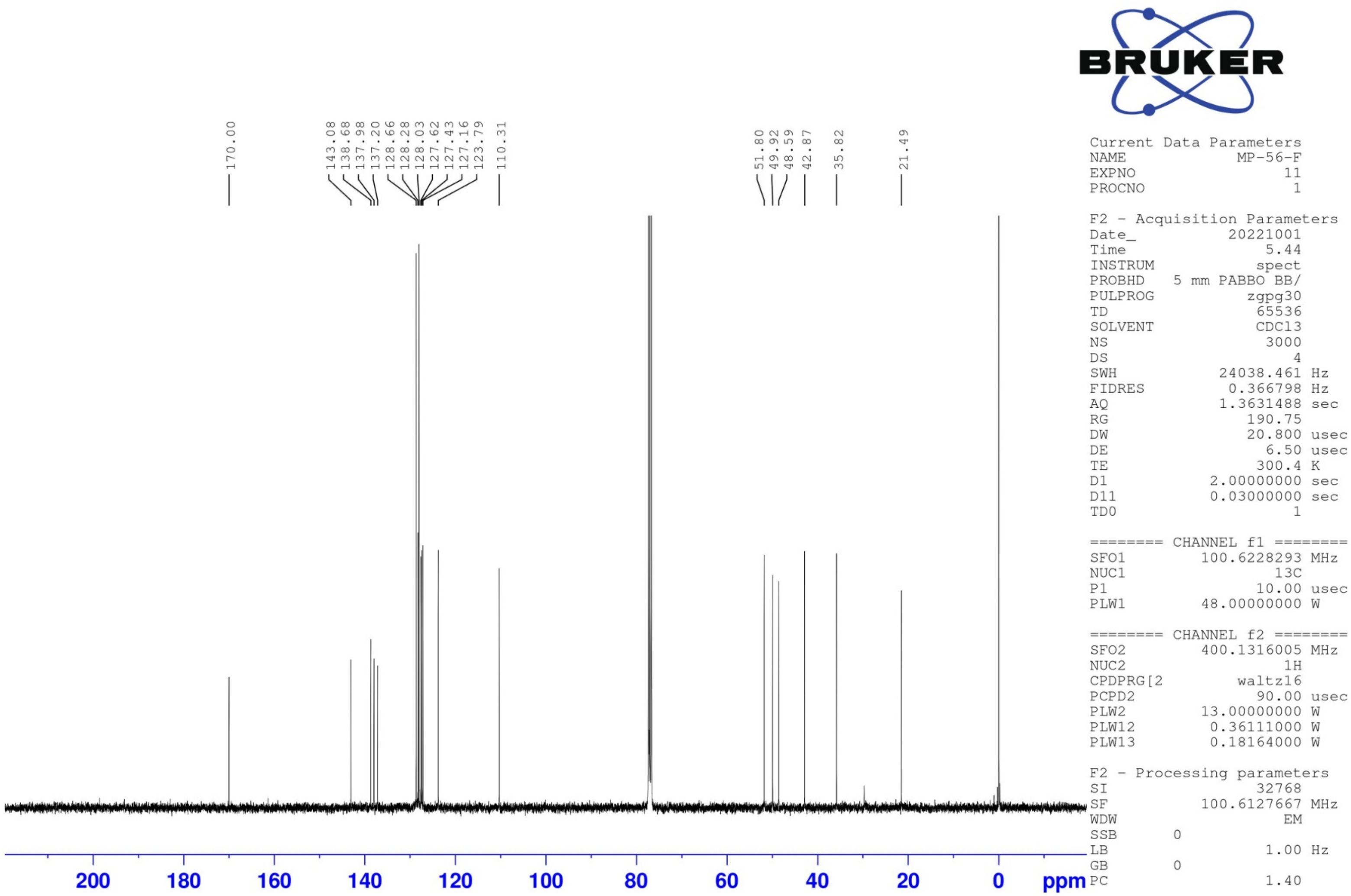
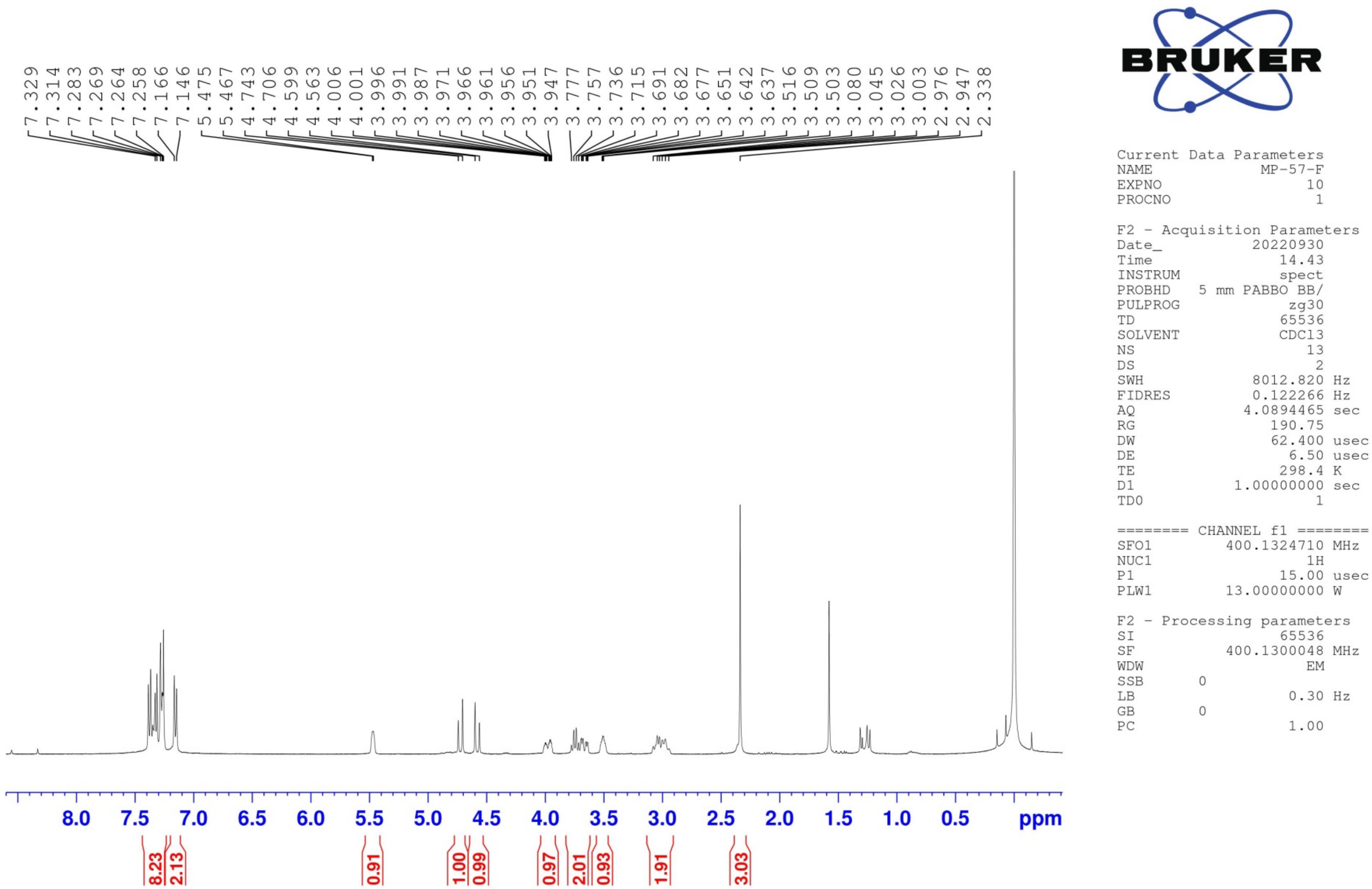
2r ^{1}H NMR spectrum (400 MHz, $CDCl_3$):



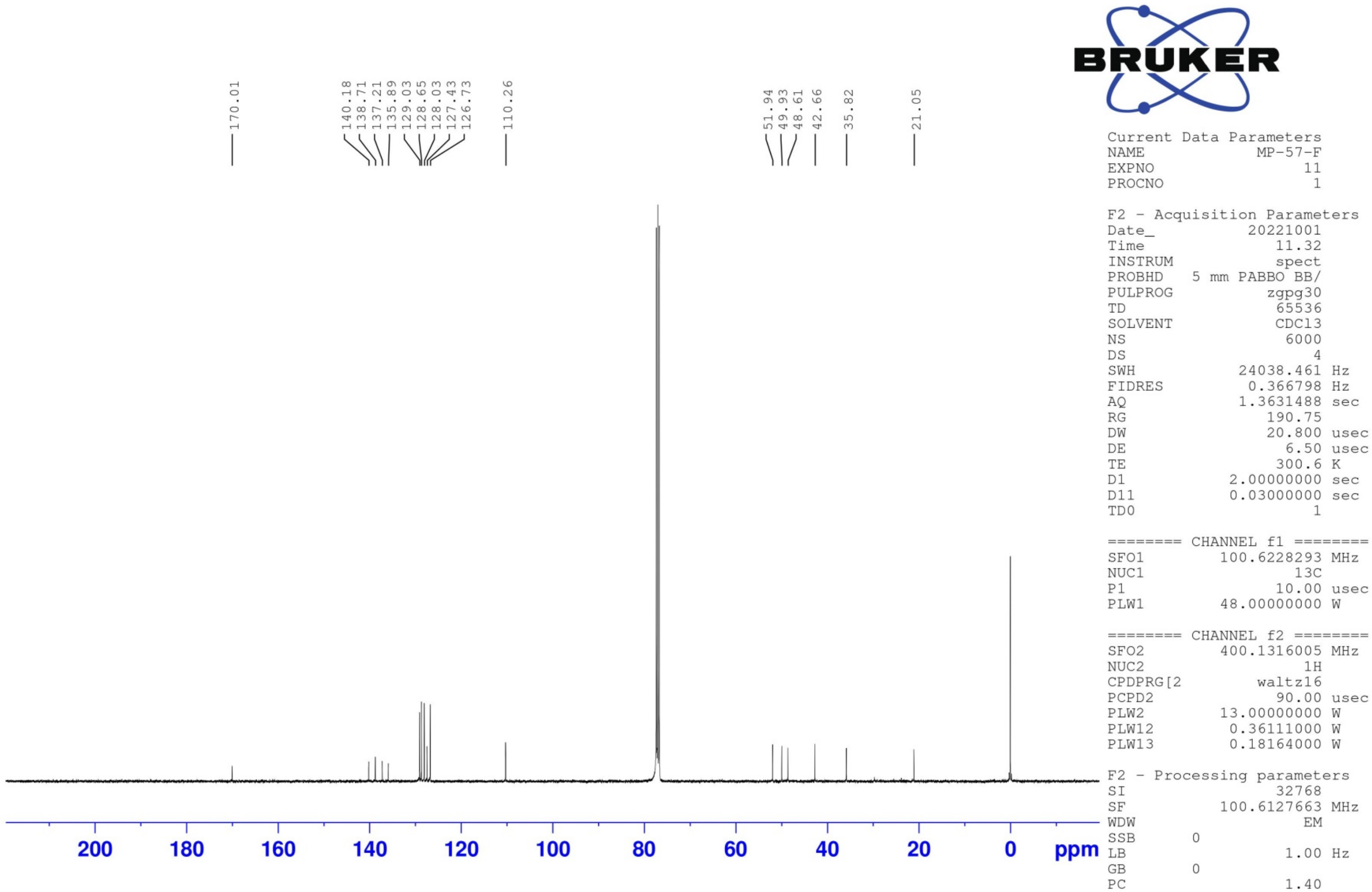
2r ^{13}C NMR spectrum (101 MHz, $CDCl_3$):



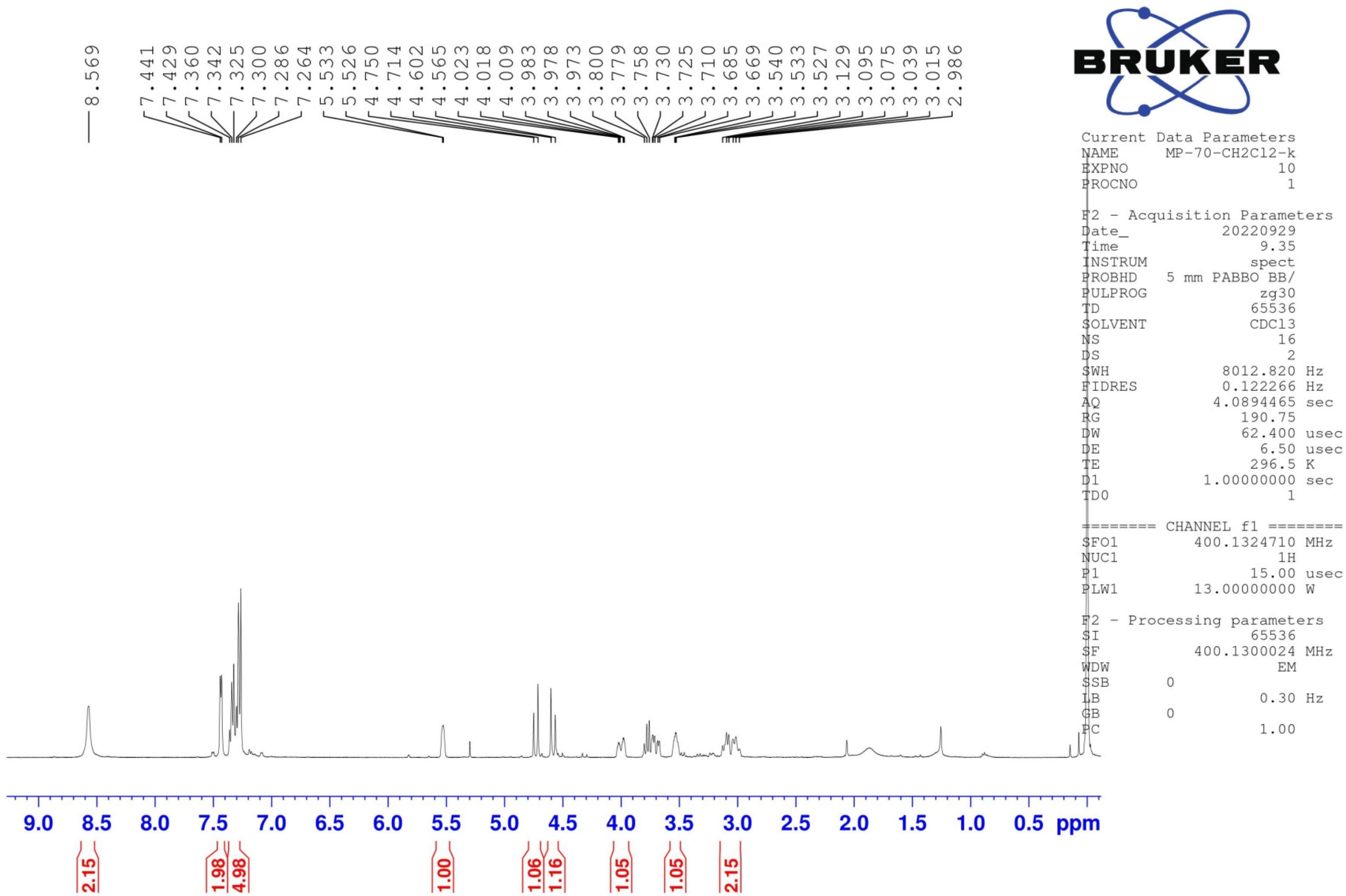
2s ^{1}H NMR spectrum (400 MHz, $CDCl_3$):



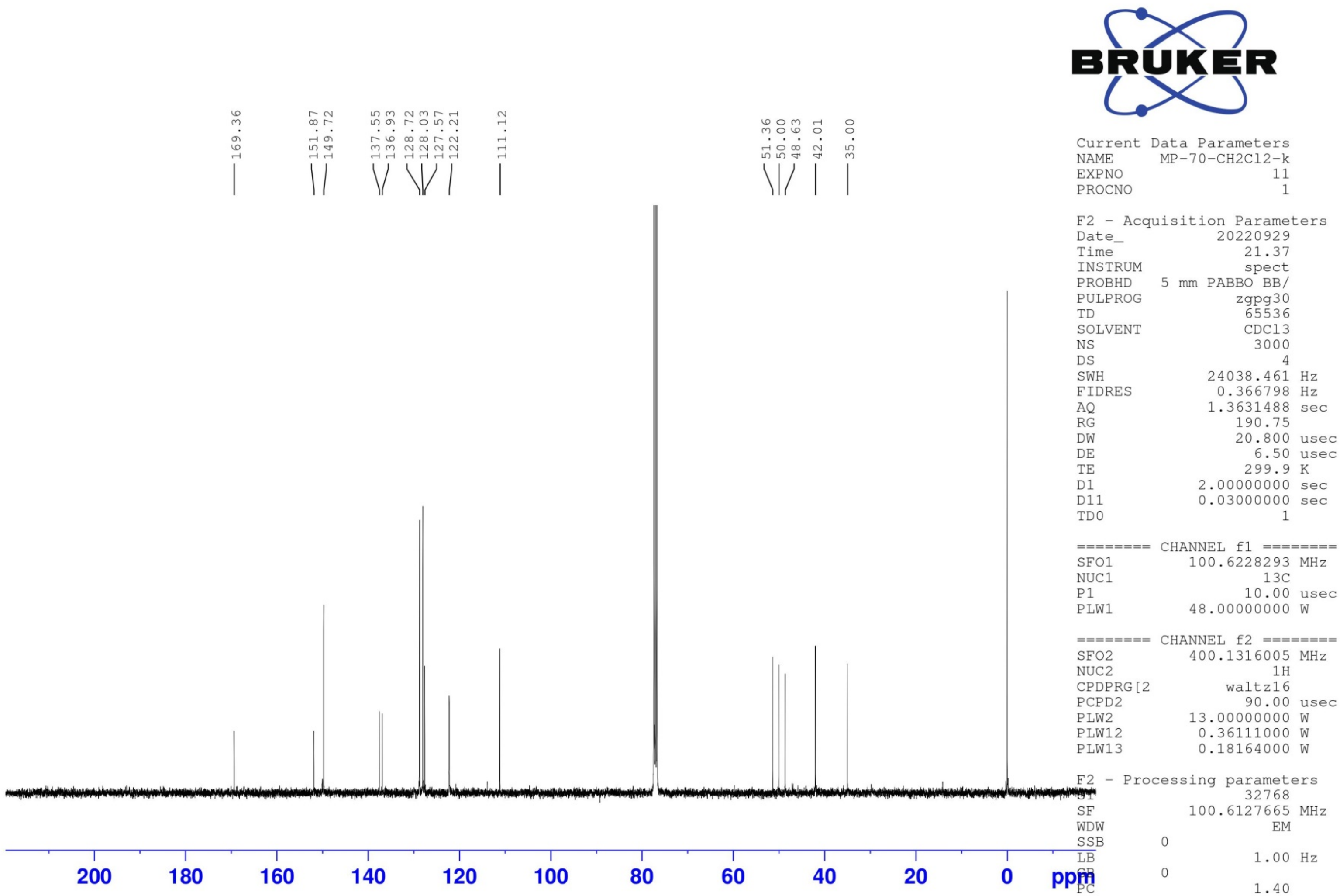
2s ^{13}C NMR spectrum (101 MHz, $CDCl_3$):



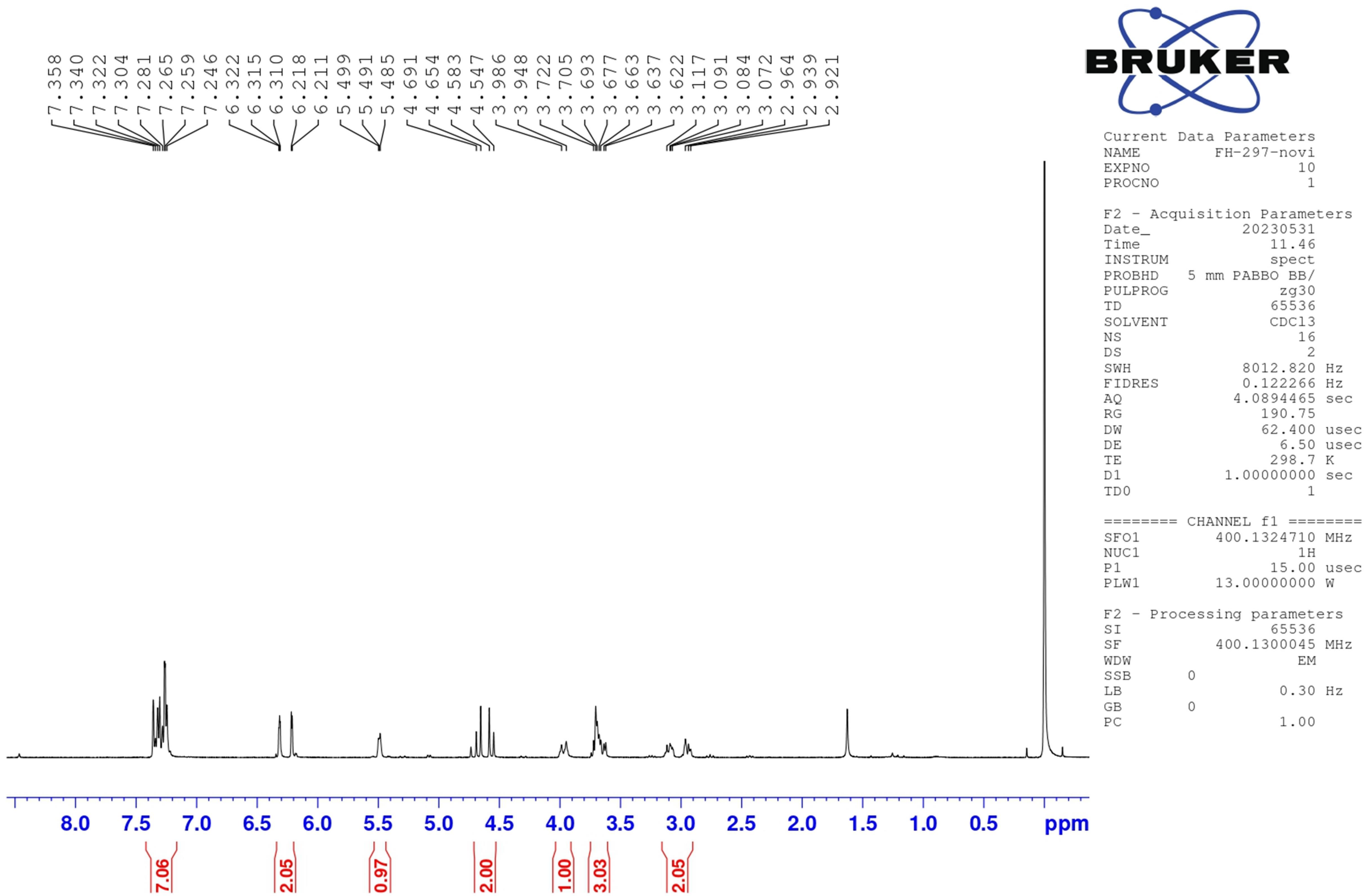
2t ^{1}H NMR spectrum (400 MHz, $CDCl_3$):



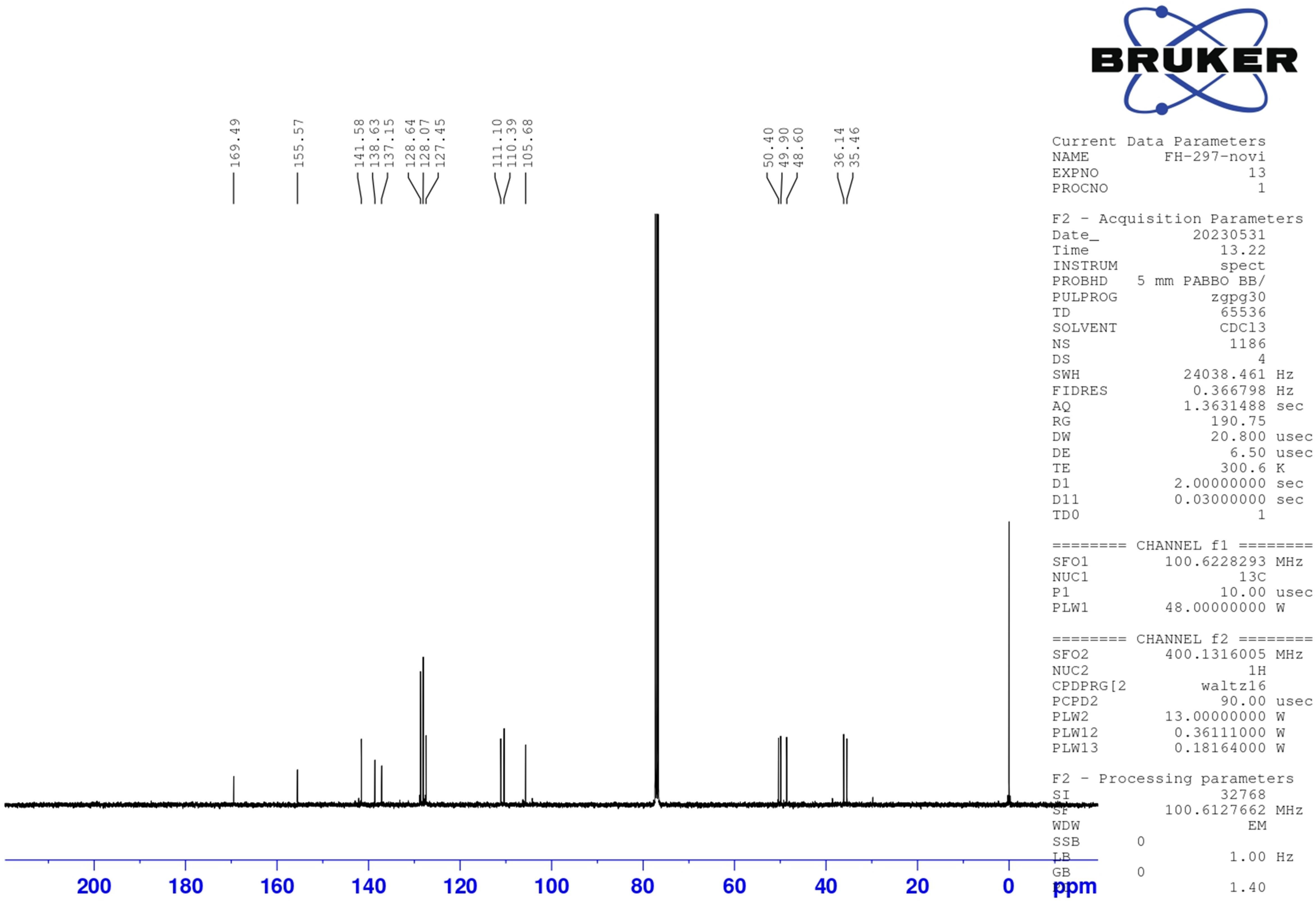
2t ^{13}C NMR spectrum (101 MHz, $CDCl_3$):



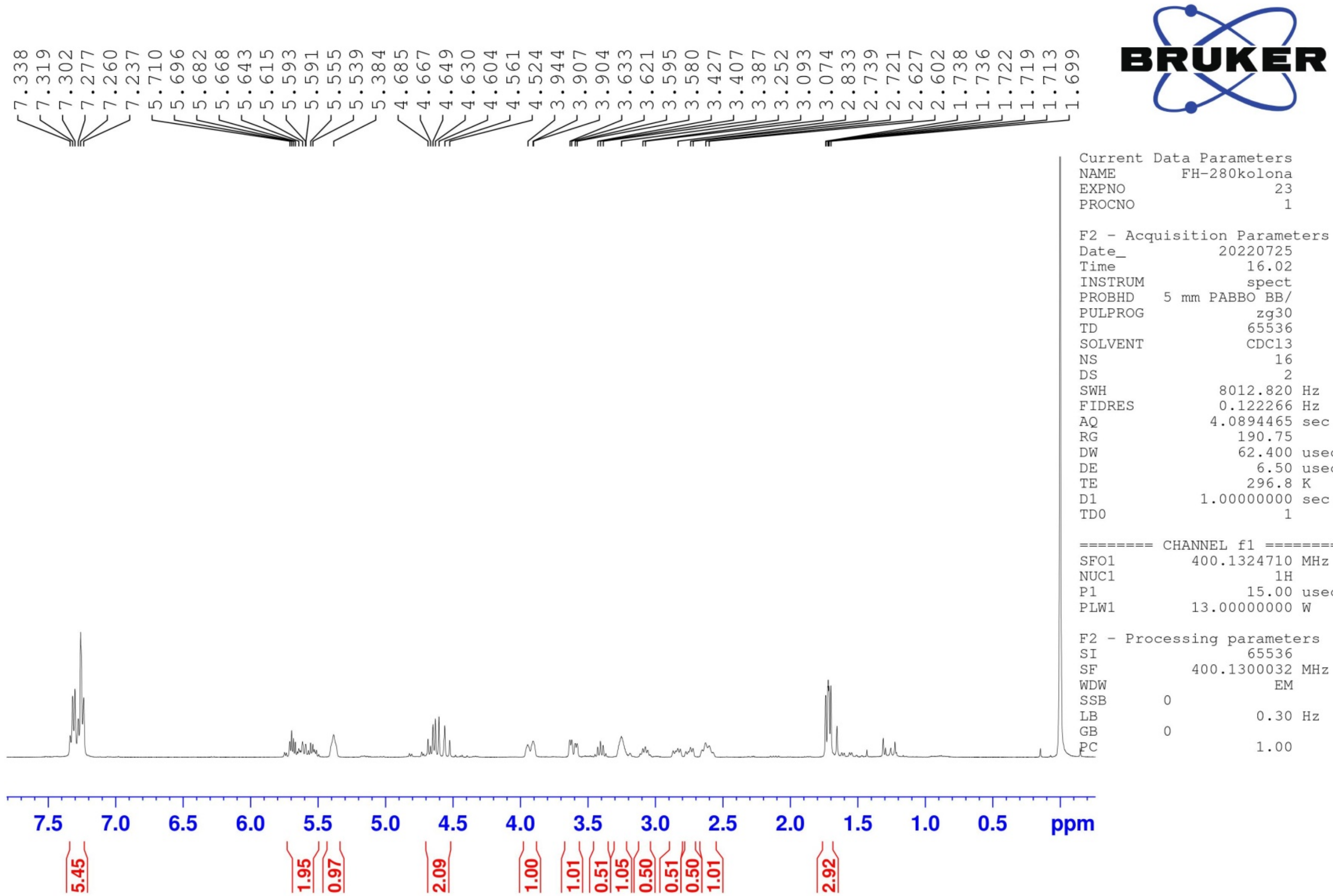
2u ^{1}H NMR spectrum (400 MHz, $CDCl_3$):



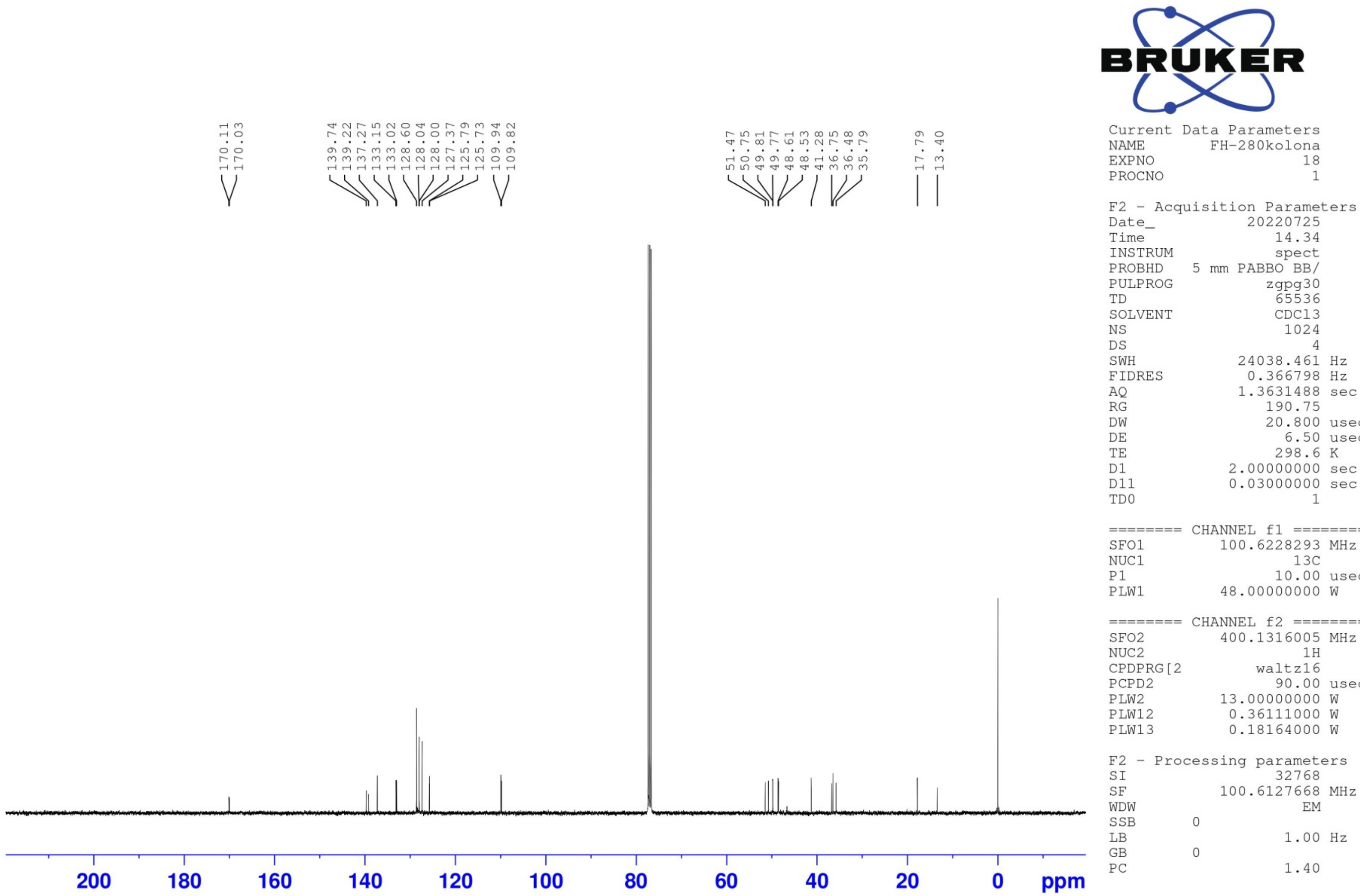
2u ^{13}C NMR spectrum (101 MHz, $CDCl_3$):



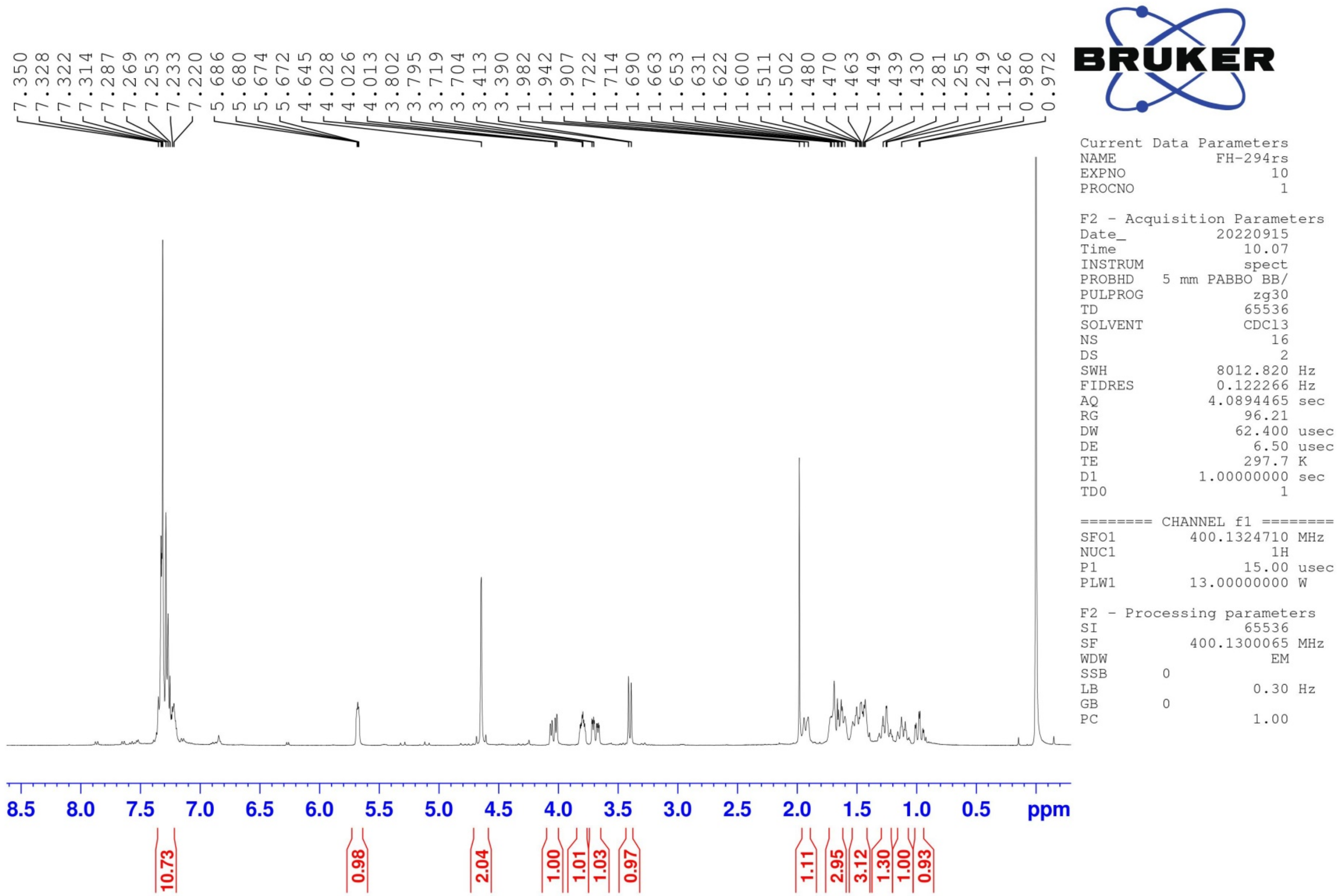
2v ^{1}H NMR spectrum (400 MHz, $CDCl_3$):



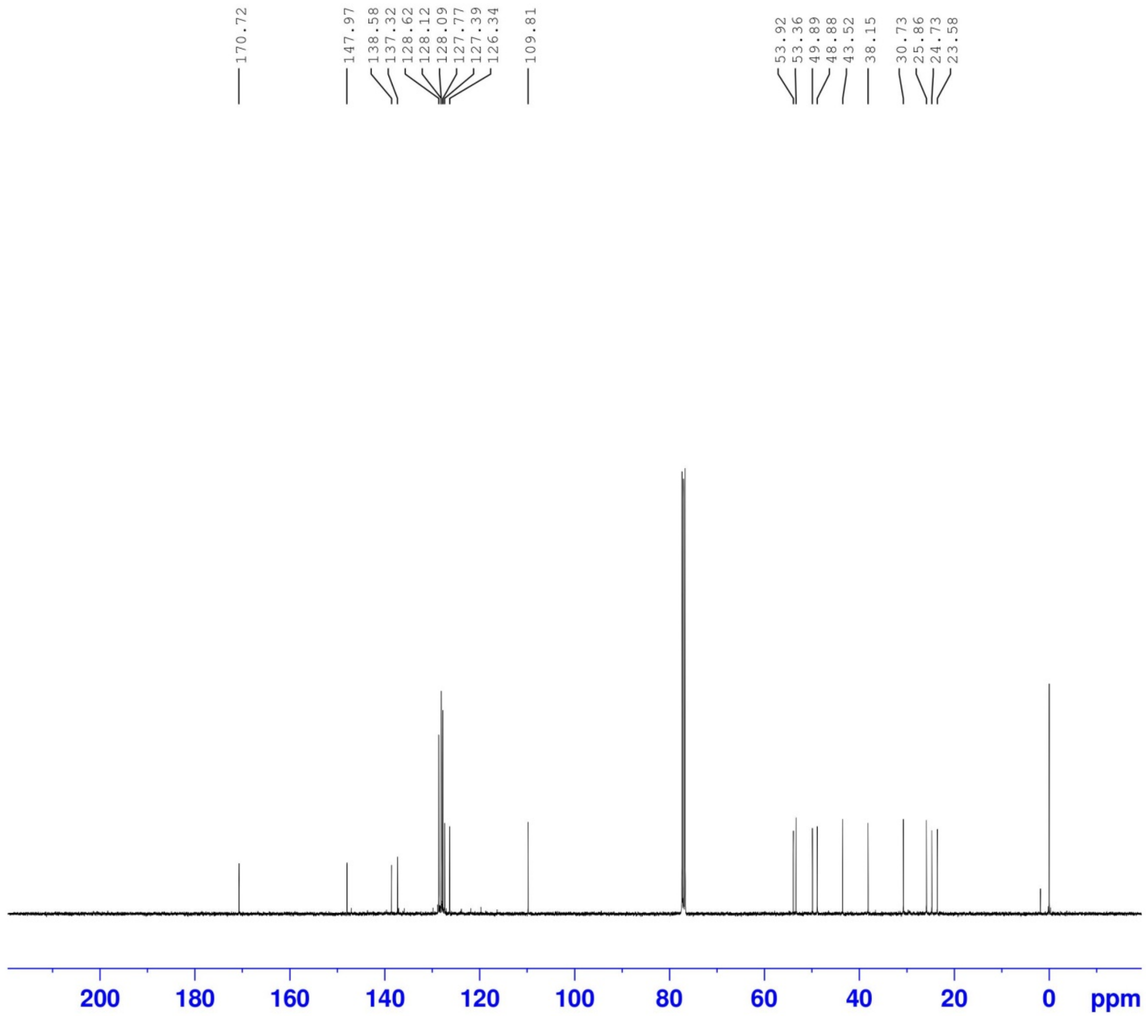
2v ^{13}C NMR spectrum (101 MHz, $CDCl_3$):



2w ^{1}H NMR spectrum (400 MHz, $CDCl_3$):



2w ^{13}C NMR spectrum (101 MHz, $CDCl_3$):

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Current Data Parameters
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EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameters
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Time                18.25
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631488 sec
RG                190.75
DW                20.800 usec
DE                  6.50 usec
TE                 299.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                 13C
P1                 10.00 usec
PLW1         48.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         13.00000000 W
PLW12         0.36111000 W
PLW13         0.18164000 W

F2 - Processing parameters
SI                 32768
SF           100.6127680 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
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